The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

An Investigation of the Reactions Leading to Volatilization of Inorganic Sulfur During Pyrolysis with Vanillic Acid and Sodium Gluconate

David T. Strohbeen

June, 1981

TABLE OF CONTENTS

ABSTRACT

The formation of volatile sulfur compounds from sodium sulfide, sodium thiosulfate, sodium sulfite, and sodium sulfate was studied during slow pyrolyses with sodium gluconate or vanillic acid. Pyrolyses were carried out at constant heating rates between ambient temperature and 550°C in a batch reactor with a nitrogen purge to continuously dilute, remove, and cool the pyrolysis product gases.

Amounts and forms of volatilized sulfur were found to depend primarily on the specific nature of the inorganic sulfur compound. The specific nature of the organic compound and the inorganic particle size were also important variables. Heating rate and nitrogen purge rate had little effect on the amount of volatile sulfur formed, although heating rate did affect the composition of the volatile sulfur product mixture.

Pyrolysis of sulfide with either organic compound gave nearly complete volatilization of sulfur as hydrogen sulfide. This is apparently due to stripping of H_2S by the H_2O and CO_2 resulting from pyrolytic degradation of the organic material. The reaction can be written:

$$Na_2S(s) + H_2O(g) + CO_2(g) \rightleftharpoons Na_2CO_3(s) + H_2S(g)$$

Sulfur volatilization from sodium thiosulfate ranged from 30 to 40% of that initially present. The residue contained a wide variety of sulfur forms including sulfide, polysulfur, sulfate, and organic sulfur. The behavior of thiosulfate during pyrolysis is best explained by a three-reaction model:

1. Low-temperature acidic degradation to sulfur dioxide and elemental sulfur:

$$2H^+ + S_2O_3^= \rightarrow SO_2 + \underline{S}^o + H_2O$$

2. Low-temperature reduction to sulfide and elemental sulfur:

$$Na_2S_2O_3 + 3CO \rightleftharpoons Na_2S + \underline{S}^o + 3CO_2$$

3. Higher temperature thermal degradation to sulfate and polysulfide:

$$Na_2S_2O_3 \rightarrow 3/4\ Na_2SO_4 + 1/4\ Na_2S_5$$

The elemental sulfur produced in these reactions reacts further to produce volatile and nonvolatile reduced sulfur compounds.

Sulfite and sulfate were essentially stable to pyrolyses except for sulfite pyrolyzed with vanillic acid. The small amount of SO_2 formed in this latter case is not unexpected, since acids will liberate SO_2 from sulfite.

The results of this study clearly indicate that different compounds behave differently during pyrolyses. Plausible mechanisms are provided to explain this behavior. These results cast strong doubt on the previous results of Douglass and Price, which showed that sulfide and thiosulfate behave similarly during pyrolysis.

INTRODUCTION

Efficient recovery of pulping chemicals and thermal energy from black liquor is essential to the economic success of the kraft pulping industry. The most acceptable current recovery technology involves the Tomlinson recovery furnace. Spent pulping liquor, containing inorganic pulping chemicals and dissolved wood substances, is concentrated to 60-70% solids and sprayed into the furnace. Within the furnace the liquor undergoes final evaporation and stripping of volatile organics, pyrolysis, gasification, and combustion. Heat released by combustion of the organics is used to generate steam. The inorganics, sodium sulfide and sodium carbonate, collect as a molten smelt at the bottom of the furnace. This smelt is drained from the furnace and dissolved in water. The resultant liquor is then treated with calcium oxide to convert the carbonate to hydroxide. With removal of the calcium carbonate precipitate, the liquor is ready for reuse in the pulping operation.

Though the objective of chemical recovery is adequately achieved, there are serious drawbacks associated with the recovery furnace. In general, since so many processes are occurring within the furnace, it is difficult to optimize or even control the processes. Specific drawbacks include the ever-present danger of smelt-water explosions, malodorous and particulate atmospheric emissions, and energy inefficiency.

Recovery research can have two distinct aims. It can aim at increased understanding of the events occurring within a conventional recovery furnace in order to exert greater control over furnace operation, or it can aim at the development of alternative recovery technologies that would replace the furnace. However, whether dealing with a furnace-centered or an altogether new recovery technology, the basic raw materials, recovery objectives, and types of reactions do not change. Liquor

organics must be broken up and oxidized; sulfur compounds must be reduced to sulfide for reuse in the pulping cycle.

Pyrolysis, irreversible thermal decomposition, is a key step in any conceivable recovery operation, affecting the recovery of both pulping chemicals and thermal energy. Kraft black liquor pyrolysis results in the formation of combustible volatiles and a carbonaceous char containing sodium salts. During pyrolysis much of the sulfur present in the black liquor is volatilized. The distribution of sulfur between solid and gaseous phases is important. Reduced sulfur compounds resulting from pyrolysis are malodorous federally regulated pollutants, and any sulfur lost as an atmospheric emission must be replaced at additional cost. Knowledge of the factors influencing the sulfur distribution would increase understanding of the sulfur cycle within the furnace, leading to an increased ability to control furnace behavior.

At present there is little information on how various black liquor sulfur compounds behave during pyrolysis. The reactions leading to formation of volatile sulfur compounds are unknown. The objective of this thesis study was to investigate the reaction mechanisms leading to the formation of gaseous sulfur compounds from inorganic sulfur salts during kraft black liquor pyrolysis.

LITERATURE REVIEW

PYROLYSIS

Pyrolysis refers to the irreversible thermal decomposition which takes place during heating of most substances. It should not be confused with gasification or combustion reactions, which require the additional presence of oxygen. Though pyrolysis is usually associated with fragmentation reactions, many substances polymerize upon heating. These polymerizations are also properly considered as pyrolytic decompositions.

Pyrolysis of complex substances such as wood, cellulose, and coal consists of competing fragmentation and polymerization reactions. Their pyrolysis kinetics are characterized by several stages (1). The stages include an initial slow induction period, a period of accelerated reaction, and the final period during which the reaction slows down. The pyrolysis kinetics are illustrated in Fig. 1.

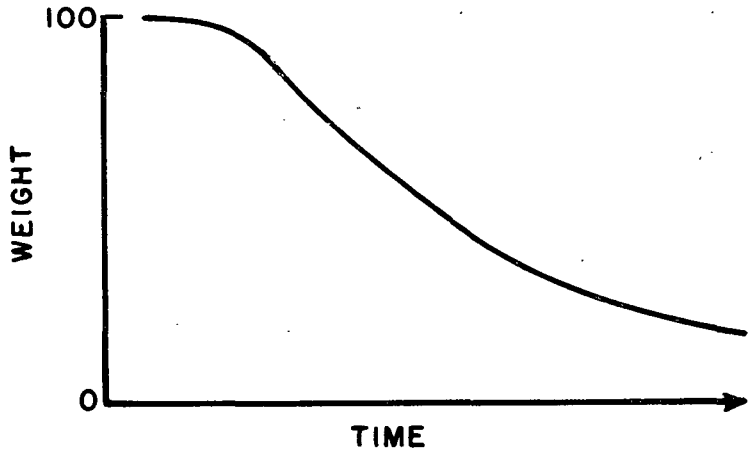


Figure 1. Typical pyrolysis kinetics at constant heating.

The pyrolysis products of the complex substances mentioned above are remarkably similar, consisting of volatile products and a nonvolatile coke or charcoal. The volatiles can be further subdivided into noncondensible gases, primarily CO, CO_2,

H_2, and CH_4; a condensible aqueous phase; and a condensible organic tar. These products may be primary or secondary, depending upon whether they form directly from the pyrolysis substrate or from other degradation products, respectively.

THERMODYNAMICS AND KINETICS

An important aspect of pyrolysis reactions is whether thermodynamic or kinetic control is operative (2). If the amounts of reaction products are determined by their relative thermodynamic stabilities, the reaction is under thermodynamic control. However, equilibrium is not achieved instantaneously during a reaction but at a rate governed by the free energies of activation. Situations can therefore arise in which the major reaction product is not the most thermodynamically stable product but that product which is formed the fastest. Under these conditions the reaction is said to be under kinetic control.

The equilibrium product composition and rate of reaction for pyrolysis are affected by temperature. The effect of temperature on reaction rate can generally be represented by the Arrhenius equation:

$$k = k_o \exp(-E_a/RT)$$

where E_a = activation energy

k_o = frequency factor

R = gas constant

T = temperature

The reaction rate always increases with temperature, since the activation energy is always positive. The extent of the rate increase, however, is dependent on the size of the activation energy. The larger the activation energy, the more sensitive the rate is to temperature change.

The effect of temperature on the thermodynamic equilibrium is given by the van't Hoff equation:

$$\frac{d(\log_e K)}{dT} = \frac{\Delta H}{RT^2}$$

where H = enthalpy of reaction

K = equilibrium constant

R = gas constant

T = temperature

When integrated, this gives:

$$\log_e \frac{K_2}{K_1} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

The temperature effect, therefore, depends upon whether the reaction is endothermic ($\Delta H > 0$) or exothermic ($\Delta H < 0$). Equilibrium conversions for endothermic reactions increase with temperature ($K_2 > K_1$); the conversion for exothermic reactions decreases with increasing temperature ($K_2 < K_1$).

Pyrolytic fragmentation is expected to be an endothermic process because of the extensive bond breaking. Therefore, on the basis of thermodynamics, increased fragmentation and formation of volatiles is expected at higher temperatures. The condensation reactions leading to formation of the nonvolatile coke are expected to be exothermic reactions favored at low temperatures.

How the thermodynamics and kinetics of pyrolysis fit together is clearly seen in the case of sulfur volatilization during coal pyrolysis, which is discussed in a later section. The volatilization of black liquor sulfur during pyrolysis is expected to be analogous to that of coal.

KRAFT BLACK LIQUOR PYROLYSIS

BLACK LIQUOR COMPOSITION

Kraft black liquors are viscous dark liquids resulting from the digestion of wood (composed of cellulose, hemicellulose, lignin, and extractives) with an aqueous solution of sodium hydroxide and sodium sulfide. An elemental analysis of typical kraft liquor solids is given in Table I.

TABLE I

ELEMENTAL ANALYSIS OF A TYPICAL KRAFT BLACK LIQUOR
WEIGHT % OF DRY LIQUOR SOLIDS (3)

38.8%	Carbon
3.9	Hydrogen
35.2	Oxygen
3.4	Sulfur
18.7	Sodium

During kraft pulping about 50% of the wood substance enters into solution (4). This dissolved wood substance originates primarily from the wood hemicelluloses and lignin and is present in the liquor as alkali lignin and hydroxy acids. The composition of kraft black liquor is presented in Table II.

TABLE II

KRAFT BLACK LIQUOR COMPOSITION (3)

Alkali lignin	30-35%
Hydroxy acids	25-35
Extractives	3-5
Acetic acid	5
Formic acid	3
Methanol	1
Sulfur	3-5
Sodium	15-20

The hydroxy acid and carboxylic acid fractions in Table II derive primarily from the alkaline hemicellulose degradation reactions occurring during digestion. These

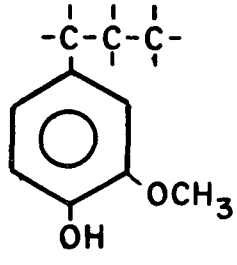
fractions contain many different acids, as shown in Table III. The major differences between hardwood and softwood acid composition (Table III) are due to the types of hemicelluloses; hardwoods are richer in xylans, and softwoods are richer in mannans. No sulfur is reported to be combined with the carbohydrate degradation products present in the black liquor.

TABLE III

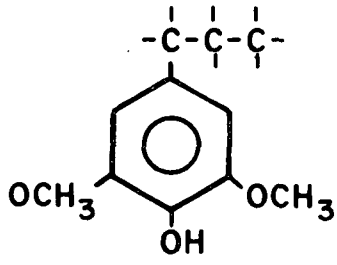
COMPOSITION OF THE CARBOXYLIC ACID MIXTURE IN PINE AND BIRCH BLACK LIQUORS (5)

	Relative Composition, %	
	Pine Liquor	Birch Liquor
Formic	16.2	12.1
Acetic	11.4	28.9
Glycolic	3.2	4.1
Lactic	10.7	10.6
2-Hydroxybutanoic	4.3	15.9
2,5-Dihydroxyvaleric	2.7	2.0
Xyloisosaccharinic	4.1	11.4
Glucoisosaccharinic	38.7	9.0
Miscellaneous acids	8.7	6.0
	100.0	100.0
Total amount, g/liter	56.1	61.2

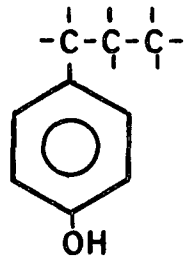
The alkali lignin originates by hydrolysis of the wood lignin. As with hemicelluloses, there is a major difference in softwood and hardwood lignin composition. Softwood lignin is considered a polymer of guaiacyl propane type monomers; hardwood lignin also contains syringyl propane and p-hydroxy phenyl propane type units (6-8):



guaiacyl propane



syringyl propane



p-hydroxy phenyl propane

Lignin hydrolysis reactions occurring during pulping yield a more complex mixture of products than the carbohydrates (8,9). The major portion of lignin, 80-85%, is solubilized as large colloidal molecules; the remainder is dissolved as relatively small molecules (4). Some sulfur is associated with the lignin degradation products.

The extractives, mentioned in Table II, are mainly resin and fatty acids. These are present in the black liquor as sodium salts.

The sodium and sulfur, listed in Table II, originate in the pulping liquor. Black liquor sodium is associated with alkali lignin, hydroxy acids, extractives, and the inorganic anions.

Black liquor sulfur can be either organic or inorganic. The inorganic sulfur is present as sulfide (S^{-2}), polysulfide (S_x^{-2}), thiosulfate ($S_2O_3^{-2}$), sulfite (SO_3^{-2}), and sulfate (SO_4^{-2}) (3,4). The organic sulfur is present as thiolignin (4,10,11), methyl mercaptan (CH_3SH), methyl sulfide ($(CH_3)_2S$), and methyl disulfide ($(CH_3)_2S_2$) (11-14). Calculations based on data from references (8) and (13) indicate that about 10% of the black liquor sulfur is organic sulfur, 2-3% thiolignin, 1-3% methyl mercaptan, 1-5% methyl sulfide, and less than 0.5% methyl disulfide. The remaining 90% of the sulfur is inorganic and is present as sulfide (35-45%), thiosulfate (20-35%), sulfite (2%), and sulfate (15-25%) (4). All of the organic sulfur compounds result from reaction between lignin and sulfide (10-14) during pulping.

The pyrolysis behavior of black liquor would be expected to be very complicated because of its complexity as a mixture. Like other complex substances, black liquor probably pyrolyzes via competitive fragmentation and polymerization reactions yielding volatile and nonvolatile products as described earlier. However, since black liquor is a mixture, there may be some nonadditive effects during pyrolysis; nonadditive effects are those that arise due to interactions between the different components. For example, the formation of volatile sulfur compounds from the

inorganic sulfur compounds during black liquor pyrolysis must involve the decomposition of the organic compounds. One nonadditive effect might be the influence of the inorganics on the pyrolytic decomposition of the organics.

Black liquor pyrolysis mechanisms have not been studied, and so little is known about them. The pyrolysis of wood, wood components, hydroxy acid, and coal have been extensively studied and are discussed in the following sections. The pyrolysis mechanisms of these substances are very complex and not well understood. However, trends exist which are present during the pyrolysis of all these materials. As discussed earlier, the pyrolysis of a material may be either kinetically controlled or thermodynamically controlled. It is not thought that different chemical compounds would pyrolyze by similar reaction mechanisms, so the trends observed during pyrolysis of these different compounds indicate the influence of thermodynamics. Black liquor has an organic composition analogous to that of these other substances and must obey the same thermodynamic laws. Therefore, some of the pyrolysis behavior of black liquor can be extrapolated from these other studies.

Of primary importance to this study are the reactions leading to the formation of volatile sulfur compounds from the black liquor inorganic sulfur salts during pyrolysis. These volatilization reactions are expected to be functions of both the organic and inorganic pyrolysis behaviors. Coal is a material containing inorganic sulfur that has been extensively studied. The behavior of coal sulfur during pyrolysis should shed light on sulfur volatilization during black liquor pyrolysis.

CELLULOSE PYROLYSIS

Slow heating of cellulose at temperatures below 240°C produces an aqueous distillate containing organic acids and noncombustible, noncondensible volatiles (15,16). Above about 240°C, pyrolytic depolymerization occurs with formation of a

tarlike substance and violent evolution of gases. The reaction is most violent between 270°C and 350°C. Further heating results in the slow distillation of products such as CO, CH_4, and H_2; the process eventually ends, leaving a cokelike residue.

Table IV (a) lists the dry distillation or pyrolysis yields of cellulose from different sources. Tables IV (b) and (c) give a more complete analysis of the nonvolatile and volatile pyrolysis products, respectively. The product composition and product yields are all similar. Any differences that do exist are probably due to impurities, since changes in degree of polymerization or crystallinity are not observed to greatly affect cellulose pyrolysis behavior (15,17). The principal volatile products are H_2O, CO_2, and CO.

Cellulose degrades pyrolytically by a complex series of parallel and consecutive reactions (15-18). However, there appear to be two general pathways, as depicted in Fig. 2. The first pathway primarily involves dehydration and polymerization reactions leading to char formation and production of noncombustible volatiles; the other pathway involves fragmentation reactions and formation of combustible volatiles. High heating rates enhance the production of combustible volatiles whereas slower heating promotes char formation and production of noncombustible volatiles.

At lower heating rates, cellulose undergoes dehydration and direct polymerization to yield cross-linked cellulose (15,17). At high heating rates, levoglucosan (1,6,β-D anhydroglucopyranose) is the principal primary reaction product (15,17,19). Cellulose decomposes to levoglucosan via a prior partial depolymerization (15-17,20, 21). Pyrolysis does not proceed through depolymerization to glucose, since glucose pyrolysis yields low amounts of levoglucosan (21). Levoglucosan formation is reduced or hindered by the presence of water-soluble impurities and lignin (16).

TABLE IV (a)

CELLULOSE DRY DISTILLATION YIELDS (15)

Product	% Yield from the Following Kinds of Cellulose				
	Cotton	Pine	Spruce	Birch	Beech
Charcoal	38.8	36.9	34.8	33.39	32.9
Water	34.5	34.2	30.0	29.35	31.9
Carbon dioxide	10.4	12.8	11.9	11.14	12.0
Carbon monoxide	4.2	3.4	3.9	3.49	3.8
Other products	12.3	12.7	18.2	22.23	18.5

TABLE IV (b)

ELEMENTARY COMPOSITIONS OF THE ABOVE CELLULOSE CHARCOALS

Type of Cellulose	% C	% H	Caloric Value, cal/g
Cotton	81.8	3.9	7,550
Pine	81.7	3.6	7,590
Spruce	81.3	4.2	7,750
Birch	83.7	4.3	7,980
Beech	83.1	4.1	7,840

TABLE IV (c)

VOLATILE COMPOSITION

Product	Percentage by Weight				
	Cotton	Pine	Spruce	Birch	Beech
Gases: CO_2	10.35	12.83	11.94	11.14	11.96
C_2H_2	0.17	0.21	0.19	0.41	0.25
CO	4.15	3.40	3.92	3.49	3.80
CH_4	0.27	0.27	0.22	0.47	0.39
Methanol	--	trace	0.07	--	0.19
Acetone	0.07	0.08	0.13	0.15	0.26
Acetic acid	1.39	2.18	2.79	3.89	3.50
Tar	4.18	4.85	6.28	9.58	5.23
Unknown organic substances	5.14	4.22	8.50	7.72	8.67
Water	34.52	34.17	29.99	29.35	31.88
Loss	0.94	0.86	1.11	0.40	0.93

The effects of inorganic impurities on cellulose pyrolysis have been extensively studied in conjunction with the flameproofing of cellulosic materials (15,17,19,20). The presence of impurities lowers the temperature at which pyrolysis begins and

results in production of more char and noncombustible volatiles, as illustrated in Fig. 3. The mechanism for the shift in kinetics from combustible volatiles formation to production of char and noncombustible volatiles is not well understood. Important catalysts for promoting char formation include the alkali carbonates and alumina (15,17,23).

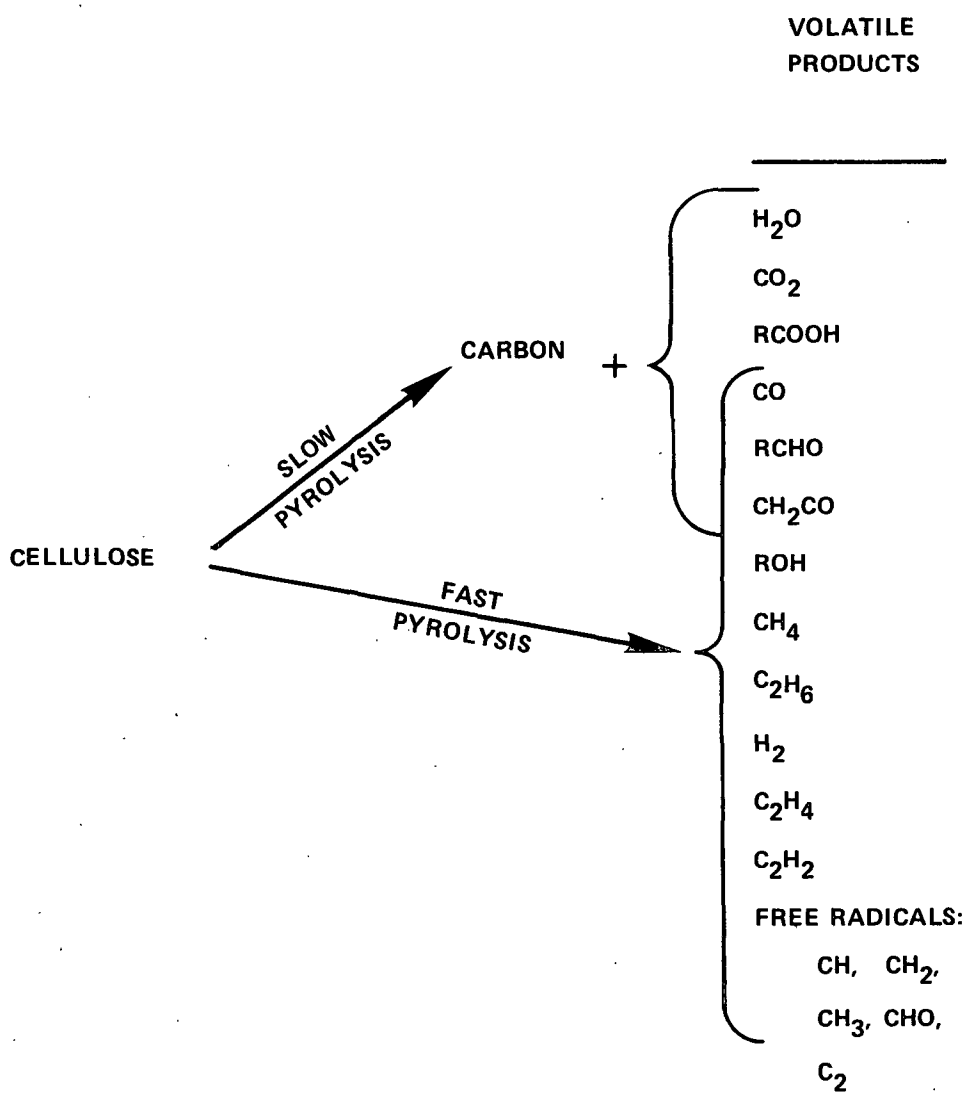


Figure 2. Cellulose pyrolysis products (16).
Heating rates typically range from 0.01°C/min to 100°C/min.

Treating cellulose with caustic solution prior to drying and pyrolysis increased the production of volatiles and decreased the quantity of residue (23). Significant

amounts of acetol (1-hydroxy propanone) and other oxygenated C_1 to C_4 compounds were produced.

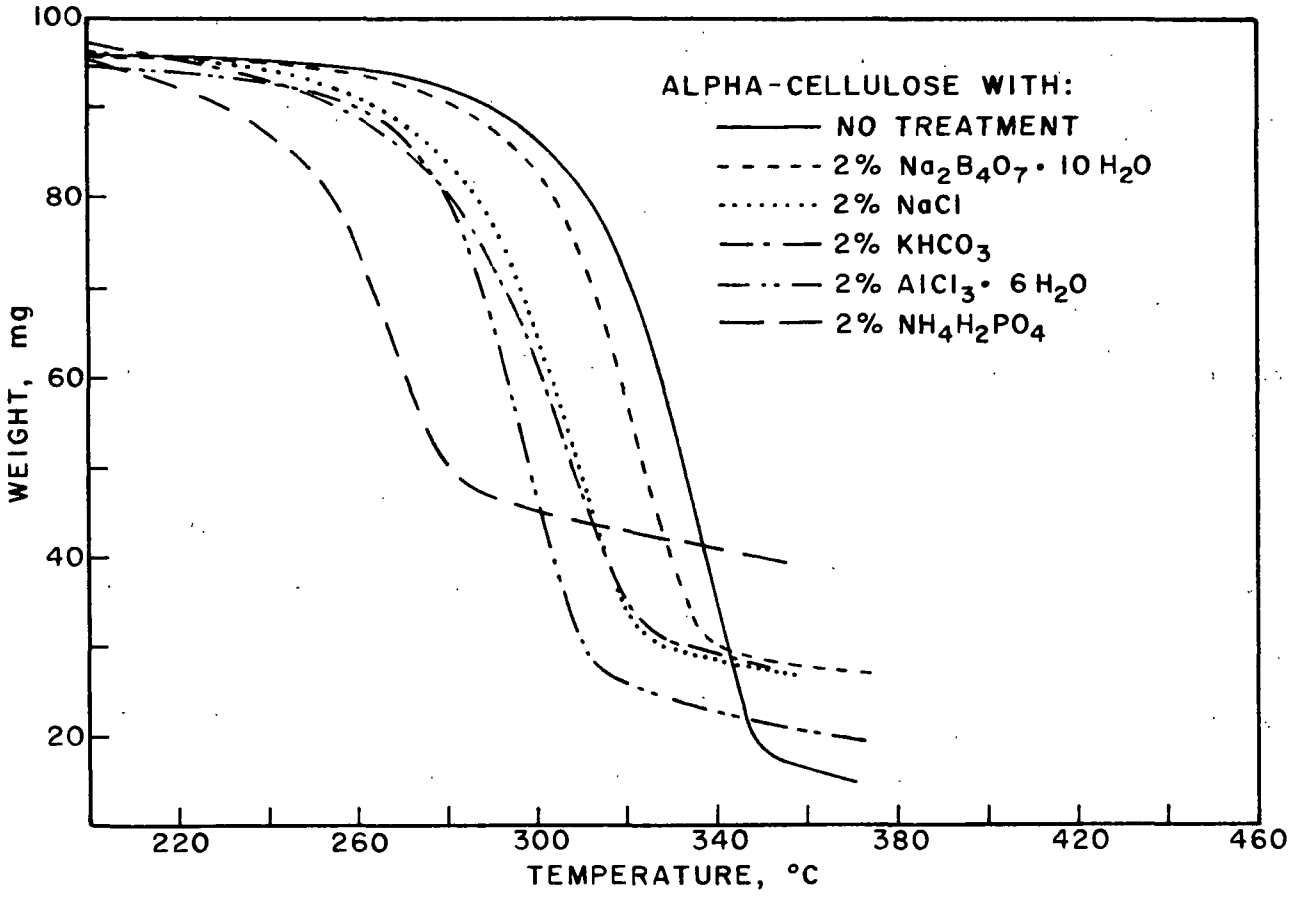


Figure 3. Relationship of increased temperature to weight of alpha-cellulose with and without inorganic salts (22).

A layer of hot char forms on the cellulose surface during pyrolysis and covers the path of volatile compounds evolving from the pyrolysis of inner materials. This char is expected to participate in secondary reactions (15), either as a catalyst or reacting material. During the later stages of pyrolysis, when the char is above 600°C, the char can react endothermically to produce H_2, CH_4, C_2H_6, etc. Hydrogen comes from the water-gas reaction:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

The other hydrocarbons form by reduction of alcohols and aldehydes originating from pyrolysis of inner materials.

The atmosphere, under which cellulose is pyrolyzed, also has an effect. Thermal degradation of cellulose in oxygen or air enhances deterioration, apparently by oxidation reactions (15). These reactions produce a "pyrocellulose" which on further heating decomposes with the evolution of H_2O, CO_2, and CO. In a closed system with the gaseous pyrolysis products remaining in contact with the cellulose substrate, there is also increased degradation (15,17). Pyrolysis under CO_2, CO, or H_2O atmospheres shows similar effects (15,17), indicating that pyrolytic degradation of cellulose in a closed system is autocatalytic.

To summarize, cellulose degradation proceeds through competing fragmentation and polymerization reactions. The polymerization reactions, favored at low temperatures and heating rates, produce char and noncombustible volatiles such as H_2O, CO_2, and organic acids. Fragmentation reactions produce combustible volatiles and are favored by rapid heating and high temperatures.

Levoglucosan is the primary fragmentation reaction product, which through further decomposition leads to the observed combustible volatiles. The presence of impurities, including many inorganic salts and lignin, inhibits levoglucosan formation by catalyzing the dehydration and polymerization reactions.

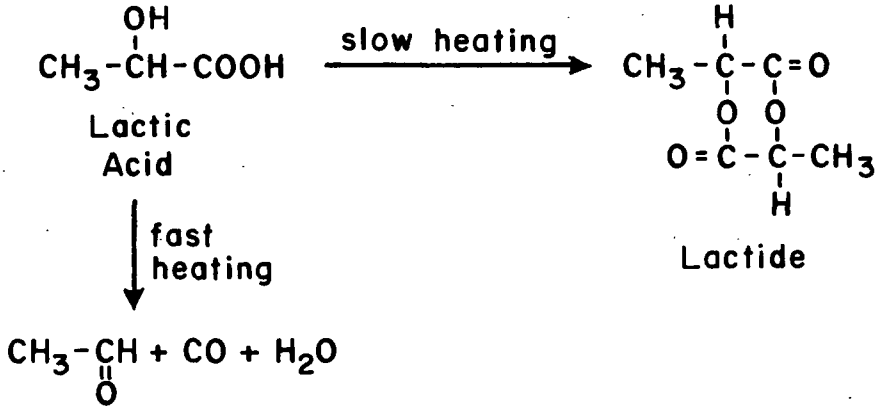
HEMICELLULOSE PYROLYSIS

Hemicelluloses start to decompose between 150°C and 200°C, and evolve more gas, less tar, and about as much aqueous distillate as cellulose (16). The hemicelluloses studied most frequently are the xylans (16,20,24-27). The pyrolysis of a xylan between 160°C and 315°C yielded 18% gas, 31.3% residue, 6.7% tar, and 43.8% aqueous distillate. The aqueous distillate contained 37% acetic acid and 32% furfural; no levoglucosan was reported (16).

Recent studies (27) indicated that the pyrolysis mechanism was a random radical chain scission. The proposed mechanism involved three processes. The chain would break at some point and then either monomer units could split off or the chain end would stabilize. The major gaseous products from 200°C to 300°C were CO_2 and CH_2OH (16).

HYDROXY ACID PYROLYSIS

Black liquor does not contain much cellulose or hemicelluloses per se, but contains primarily their degradation products, the hydroxy acids. Upon heating, hydroxy acids usually undergo intra- or intermolecular condensation, forming the lactone or lactide, respectively (2,24,28). The product depends upon molecular size and the position of the hydroxyl group (2,24). A hydroxy acid can also dehydrate to the unsaturated acid (24). Lactic acid can either dimerize by condensation to the lactide or fragment to an aldehyde, depending on temperature and heating rate (24):



LIGNIN PYROLYSIS

Lignin pyrolysis begins at around 280°C at atmospheric pressure (16). Slow structural changes occur up to about 350°C, after which rapid pyrolysis occurs, with the disappearance of oxygen-containing groups. Above 450°C, pyrolysis slows.

The principal products of lignin pyrolysis are a charcoal (55% yield), an aqueous distillate (20% yield), a tar (15% yield), and a noncondensible gas (12% yield) (29). Lignin pyrolysis produces more aromatic products and charcoal than cellulose pyrolysis (16-22,24-27,29). Lignin does not form one characteristic primary product as cellulose does. Initial breakdown occurs chiefly in the straight-chain links connecting aromatic units (16). Therefore, several primary products are formed which are closely related structurally to formulas attributable to lignin; the major products are shown in Fig. 4. The side chains produce CO_2, hydrocarbons, formic acid, acetic acid, and methanol.

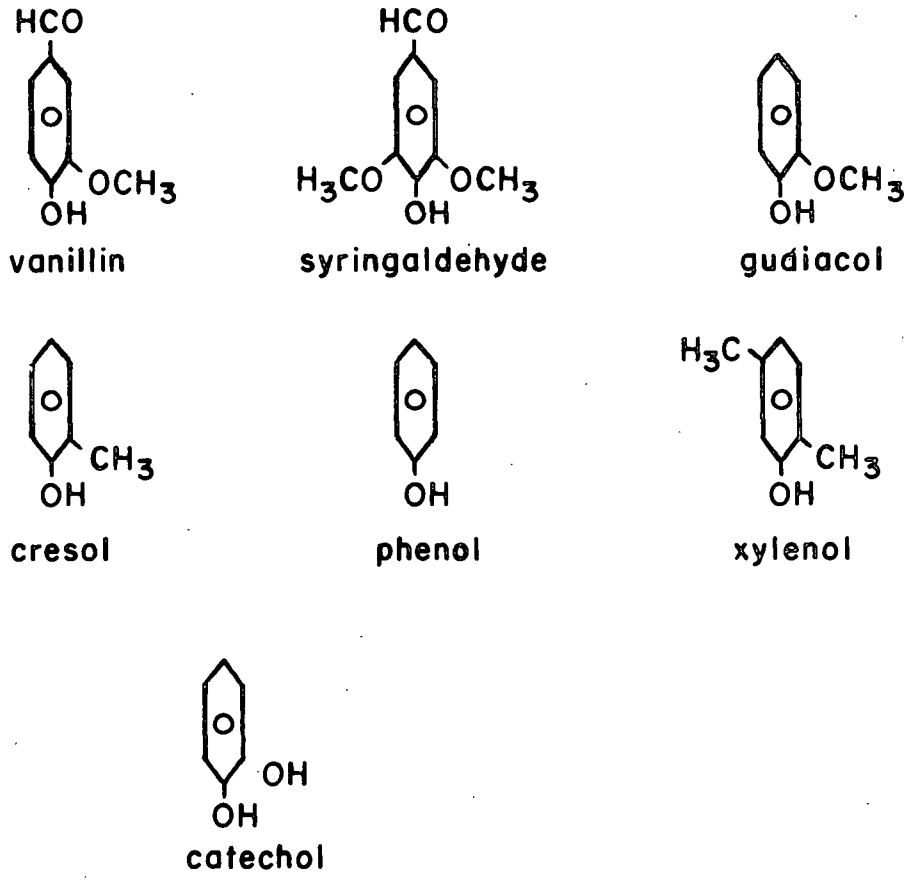


Figure 4. Products formed from aromatic nuclei.

The principal pyrolysis gases are CO, CH_4, CO_2, and H_2 (7,15,25,29). At higher temperatures and heating rates there is an increased production of unsaturated

hydrocarbons (29,30). Lignin pyrolyzed in a low-temperature plasma between 700°C and 750°C (31), producing principally acetylene (C_2H_2) and carbon monoxide.

Lignin pyrolyzes by both multicentered and radical mechanisms (32). The primary reactions leading to the initial molecular rearrangements are thought to be due to multicentered mechanisms, whereas the decompositions occur by radical mechanisms.

Lignin pyrolysis does not appear to be altered by the presence of inorganic salts (22,29), but heating rate and pyrolysis atmosphere do affect the product distribution (29).

To summarize, the pyrolytic degradation of lignin begins near 280°C. Lignin pyrolysis produces much more charcoal and aromatic products than cellulose or hemicellulose pyrolysis. There is no characteristic primary product as is true of cellulose pyrolysis. Lignin pyrolysis is not greatly affected by the presence of inorganics.

WOOD PYROLYSIS

Wood is composed of lignin, cellulose, hemicellulose, and extractives. During pyrolysis the wood behaves much as if it were a simple mixture of these compounds (16,20,22); hemicellulose reacts from 150°C to 260°C, cellulose reacts from 240°C to 350°C, and lignin reacts from 280°C (16). The pyrolysis products are noncombustible gases, pyroligneous products (aqueous distillate), tar, and charcoal (20,25,33,34). The yields of these four components as a function of temperature are shown in Fig. 5. The corresponding gas composition is shown in Fig. 6. The amount of volatiles increases with temperature, with a corresponding decrease in pyrolysis residue. Figure 7 indicates that at higher temperatures the pyrolysis gas contains a relatively higher proportion of combustibles.

Wood pyrolysis begins after the last water is removed - between 140°C and 200°C (16,20). Gases are evolved from 200°C to 500°C. The production rate of pyroligneous products passes through a maximum between 250°C and 300°C and virtually ceases at 350°C. Tars are evolved from 300°C to 450°C. The yield of wood pyrolysis products, Fig. 5 and 6, is similar to that obtained from pyrolysis of a proportional mixture of cellulose, lignin, and hemicellulose (20).

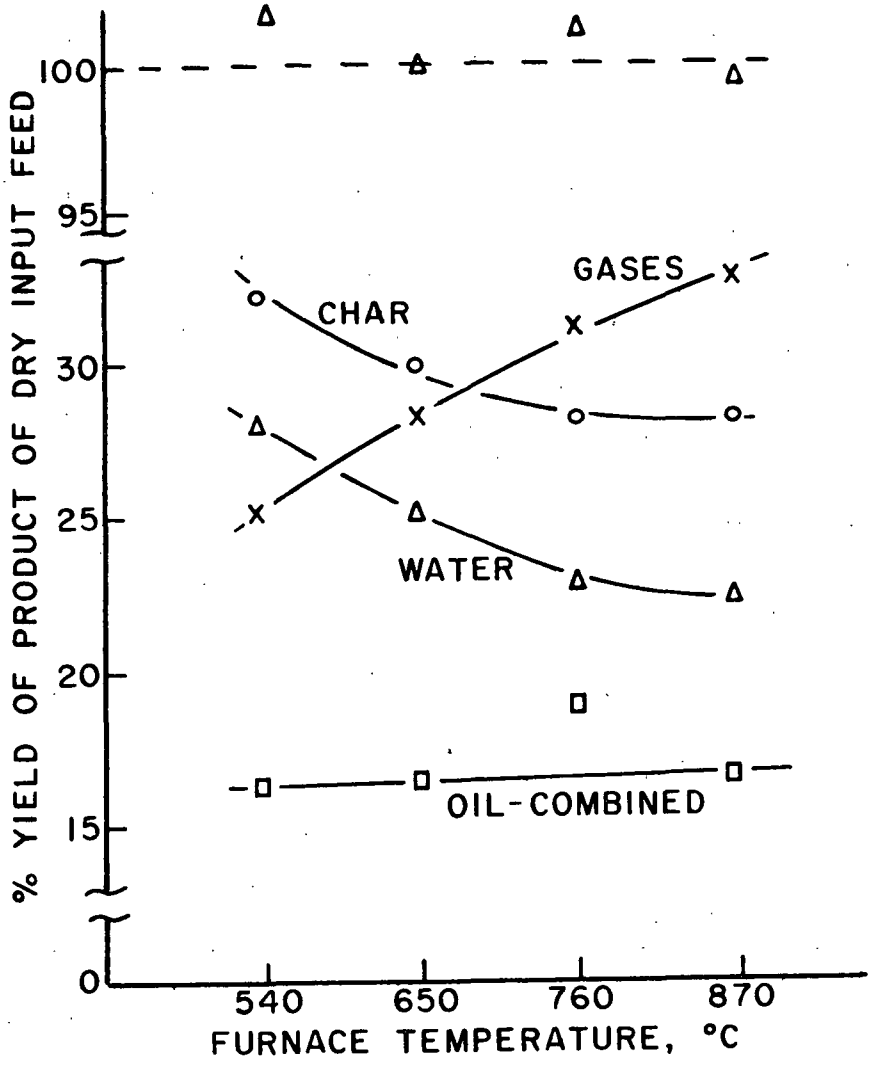


Figure 5. Yields of the four major pyrolytic products vs. temperature (34).

Thermogravimetric analysis of wood is compared with that of cellulose and lignin in Fig. 7. Wood loses weight (reacts) early, before both cellulose and lignin,

indicating that there are some synergistic effects among the various wood components during pyrolysis. One synergistic effect is the reduction of cellulose stability by interaction with hemicellulose (20).

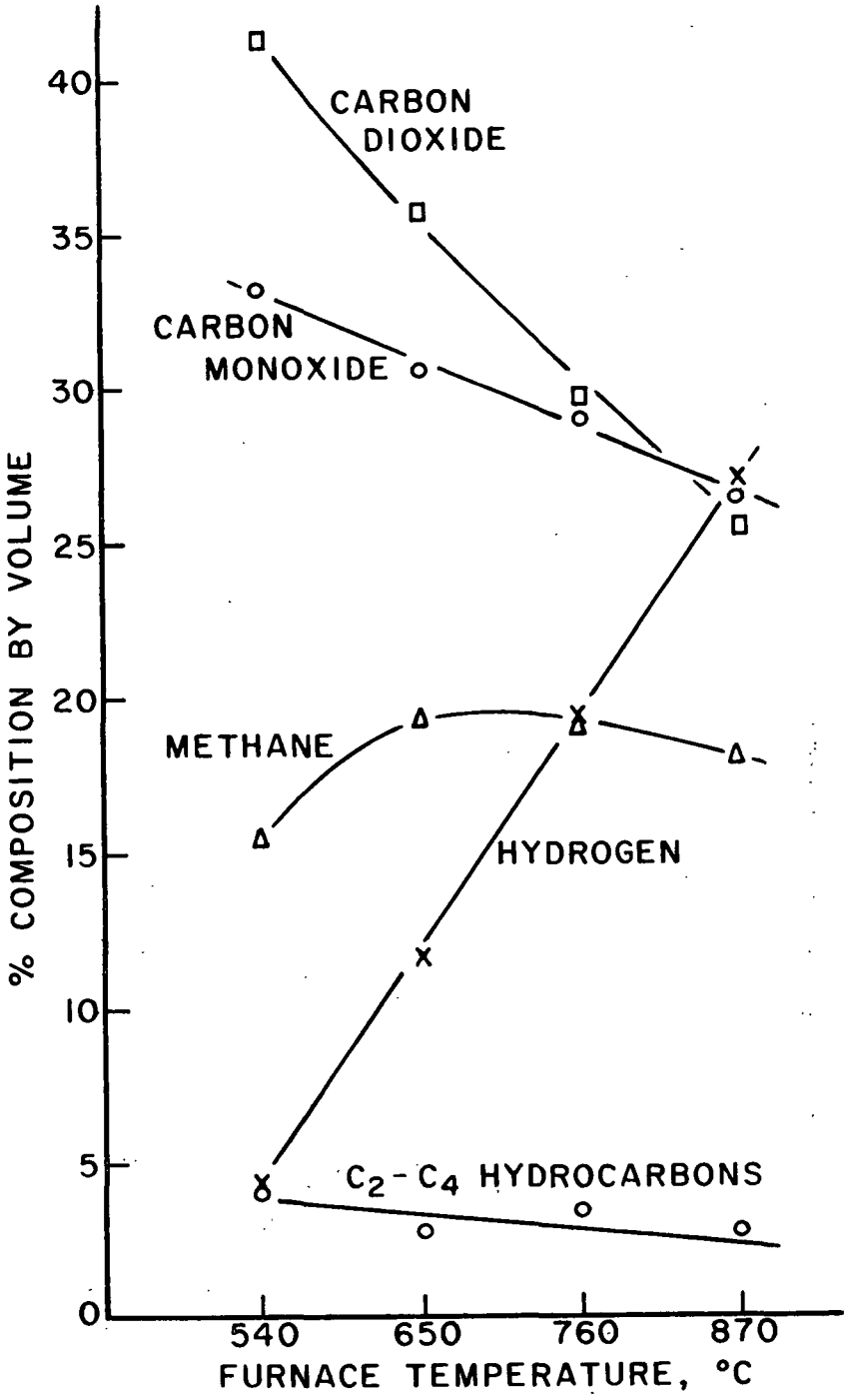


Figure 6. Variations of yields of the major gases with temperature for pine sawdust (34).

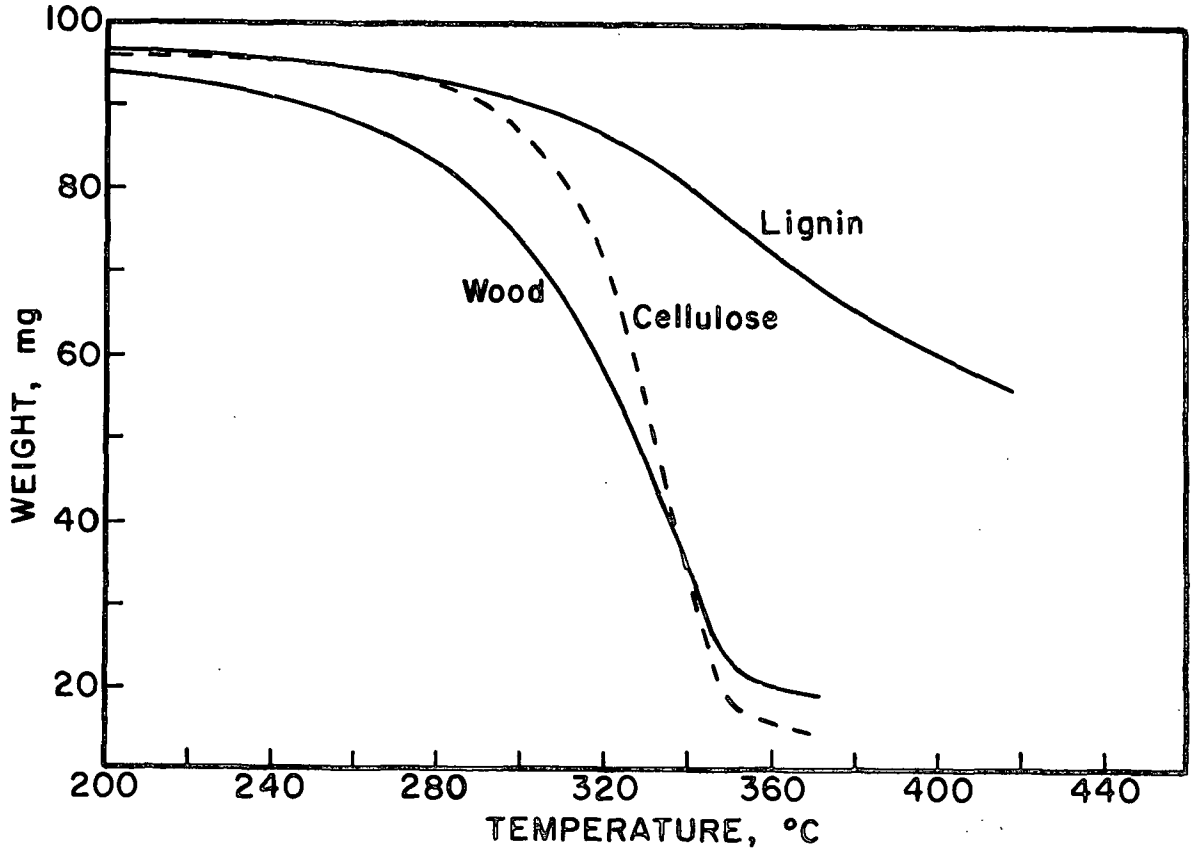


Figure 7. Results of thermal gravimetric analysis of wood, cellulose, and lignin (22).

Figure 8 presents some differential thermal analysis (DTA) curves for pyrolysis of wood and its components. In general, the contributions of the individual components can be observed in the gross features of the wood curve. For example, the low-temperature (50°C to 100°C) endothermic peak in all the wood component thermograms is observed in the thermogram for wood. Also seen in the wood thermogram is the cellulose endothermic peak at 350°C. However, the xylan peak at 250°C is found at a lower temperature in the wood thermogram; this lower temperature peak may also be due to a different reaction taking place. Other differences, including the shapes of the curves, support the idea that the pyrolysis behavior is not strictly additive.

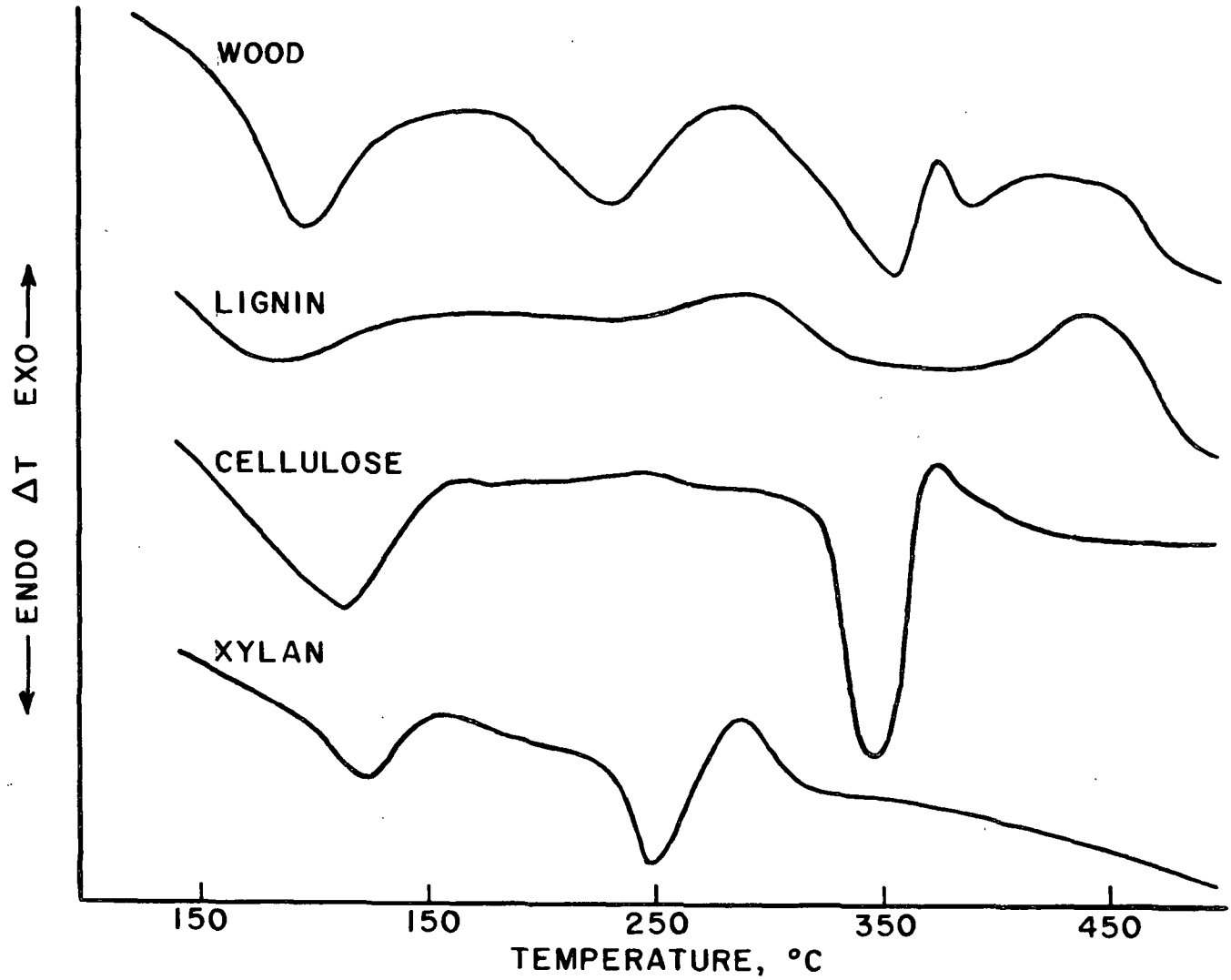


Figure 8. DTA curves for wood and its components (33).

Many factors influence the pyrolysis behavior of wood, including sample size, particle size, heating rate, atmosphere, moisture content of sample, and the presence of any organic impurities (20,22).

To summarize, pyrolysis of wood, though similar to the pyrolysis of a mixture of cellulose, lignin and hemicellulose, does present some differences. These differences are due to interactions among components during pyrolysis. Such interactions can be expected between black liquor components during pyrolysis.

COAL PYROLYSIS

Coal is a heterogeneous combustible rock formed from compaction and hardening of various plant remains and detritus. Coal pyrolysis has long been an important process for the production of coke and coal tars. The behavior of coal sulfur during pyrolysis is important to the understanding of sulfur behavior during black liquor pyrolysis.

Coal sulfur content ranges from 0.2% to 11%, though typically it is between 1% and 4% (35-37). The sulfur is classified as inorganic or organic sulfur. The inorganic sulfur consists of pyrite, marcasite, and sulfate. Both pyrite and marcasite are iron disulfide (FeS_2) and have similar chemical reactivity (35); they differ in crystalline structure. Organic sulfur is that sulfur bound to the hydrocarbon matrix as sulfides, disulfides, and thiophenes; it is all divalent sulfur. Between 50 and 80% of the coal sulfur is, in general, primarily pyrite (35,38-40). The amount of organic sulfur is usually between 30% and 50% of the total sulfur (35) but can range much higher (39). The amount of sulfate is negligible but is usually considered as ash (35-36,38-40).

The organic sulfur is evenly distributed throughout the coal (35,37,40). The pyrite occurs as particles or inclusions within the coal (35,39).

Coal begins to pyrolyze between 150°C and 200°C, with the evolution of volatiles (24). Rapid elimination of higher molecular weight paraffins and aromatics (coal oils and tars) follows at approximately 400°C. Volatile evolution gradually slows by 500°C (38), leaving a solid residue. The overall kinetics correspond to those shown in Fig. 1. The products are noncondensible volatiles, an aqueous distillate, a tar, and coke. The pyrolysis gas consists principally of CO_2, CO, H_2, and CH_4 (24,36,41), the amounts of which increase with pyrolysis temperature. This increase in gas corresponds to a decrease in tar and coke.

During coal pyrolysis the sulfur is distributed among the various product fractions, primarily between the noncondensible gases and coke (35-36,43-44). The factors that influence this distribution can be grouped as variables that are a function of the coal or variables that depend on the process. The variables included in the first group include volatile content, ash content and composition, and sulfur content and forms. The second group of variables includes heating rate, temperature, particle size, pressure, and superficial gas velocity.

The ultimate distribution of sulfur during coal pyrolysis is observed to be determined by the kinetics and thermodynamics of only H_2S (35). Most of the sulfur volatilized during pyrolysis is released below 800°C. At this temperature all the pyrite has been reduced to FeS and H_2S by reaction with the organic pyrolysis products. Ferrous sulfide (FeS) is very stable and does not readily react further (35-37,45). The reduction of FeS_2 is thought to take place at the solid-gas interface (35,45). Above 700°C the rate of back-reaction of H_2S with the basic minerals present in coal is so large that even with small contact times it is trapped (35,45). The porous structure of the coal collapses near 800°C (35,41), and further desulfurization is impossible due to mass transfer limitations (35). Sulfur volatilized above 800°C is released at a rate proportional to the volatilization of the organic material and is found as H_2S and CS_2 (carbon disulfide). In general, 50% to 70% of the sulfur present in coal is retained in the coke. The pyrolysis atmosphere greatly influences the proportion of sulfur volatilized (43).

The sulfur forms remaining in the residue are primarily organic sulfur and sulfide (FeS) (43). Some of this organic sulfur forms from the inorganic sulfur during pyrolysis (35,43).

IMPLICATIONS OF WOOD, WOOD COMPONENT, AND COAL PYROLYSIS STUDIES FOR BLACK LIQUOR PYROLYSIS

It was observed that fragmentation was favored at high temperatures and that polymerization reactions were favored at low temperatures during the pyrolysis of all the previously discussed substances. Black liquor should exhibit similar pyrolysis behavior. The first products should be volatiles, such as H_2O, CO_2, and organic acids which form at low temperatures, followed at higher temperatures by the production of noncondensible combustible volatiles.

This conclusion is very important to the volatilization of sulfur during pyrolysis. The volatilization of inorganic sulfur must involve the decomposition of the organic materials present in the black liquor. This pyrolytic organic decomposition has been shown, in all previous examples, to depend on heating rate and temperature. Therefore, the volatilization of sulfur is expected to depend on heating rate and temperature.

Hydrogen sulfide was observed to be the most important volatile sulfur form during coal pyrolysis. It was formed by reduction of the pyrite by the coal pyrolysis gases. The major portion of volatile sulfur was released below 800°C. The suppression of volatile sulfur above this temperature was due to an increasingly fast back-reaction between H_2S and the basic coal minerals and to the collapse of the porous coal structure. These results suggest kinetic control of the sulfur distribution during coal pyrolysis. Since black liquor has a composition similar to coal, the system thermodynamics should also be similar. This suggests that the black liquor sulfur distribution during pyrolysis should also be under kinetic control.

BLACK LIQUOR PYROLYSIS

Within the recovery furnace pyrolysis occurs along with gasification and combustion. Pyrolysis can be put into perspective with respect to these other processes

by single drop studies. Bjorkman (46) reports the following phases for single drops of sodium-based sulfite liquors processed at 1000°C. Upon initial exposure to hot gas, the liquor droplets slowly expand about 15%. The liquor scums over and undergoes a period of violent bursting. This bursting state is followed by a period of surface boiling after which the substance solidifies, with a slight decrease in size, into a porous mass; pyrolysis is expected to occur before and during this phase. The next phase, gasification, is accompanied by a rapid decrease in size. After gasification the mass appears to melt, vigorously boil, and eventually evaporate. The total life of the drop is approximately one second. At temperatures below 800°C no physical changes are observed after the surface solidifies and darkens; the pyrolyzed particles are porous with hollow centers. Pyrolysis of calcium sulfite liquors (47) indicates similar trends but without formation of a surface scum.

Liquor droplets pyrolyzed at high temperatures in nitrogen (46) proceed through the boiling and pyrolysis stage, leaving a black residue. It is inferred that drying and pyrolysis precede gasification and combustion and are mainly independent of them. Pyrolysis can therefore be discussed without recourse to these other processes.

Feuerstein (48-49) studied the kraft black liquor pyrolysis product distribution as a function of temperature. An aliquot of an uncharacterized black liquor sample was evaporated at low heat under vacuum. The sample was pyrolyzed at a particular temperature by heating to the desired temperature over a two-hour period. This technique changed both the heating rate and temperature and did not allow the effects to be separated.

Feuerstein reported that the pyrolysis of black liquor solids began at 250°C, preceded by a period of stripping distillation. Pyrolysis products included condensible and noncondensible volatiles and a solid residue containing sodium salts. The

condensible volatiles consisted of an aqueous fraction (pyrolysis water) and an organic liquid. The weight distributions of the products (grams product per 100 grams total solids) are plotted in Fig. 9. The most important temperature effects are the increase in pyrolysis gas and decrease in solid residue with increasing temperature. These results are similar to those shown in Fig. 5 for the product yields resulting from wood pyrolysis.

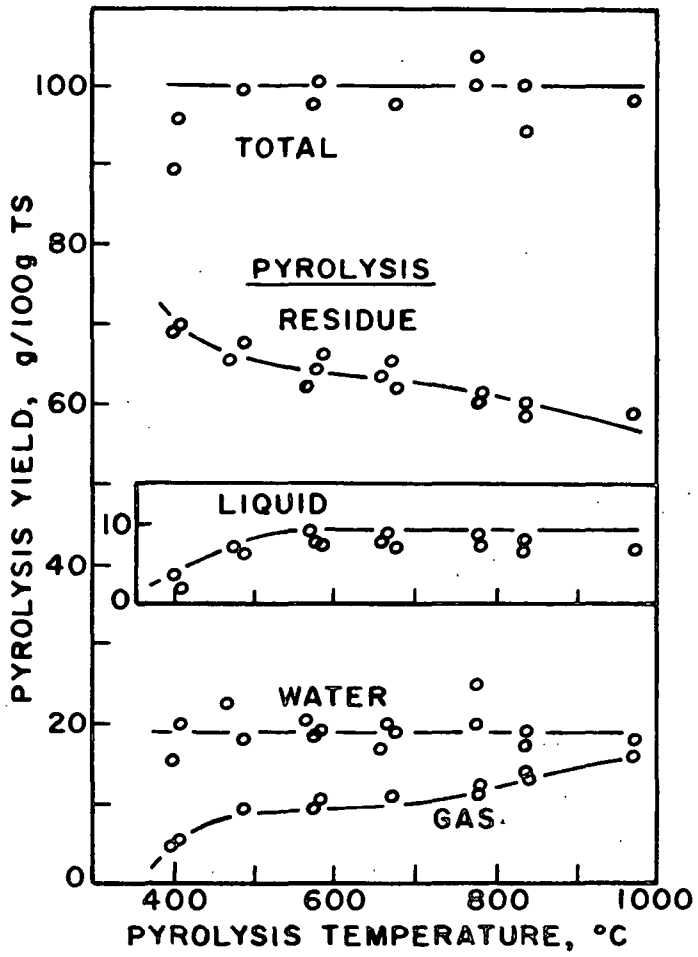


Figure 9. Batch pyrolysis product weight distribution (49).

Steady-state pyrolysis of black liquor produced results substantially different from those of Feuerstein's batch pyrolyses. For batch pyrolysis studies black liquor was evaporated and the solids then brought to the final pyrolysis temperature in two hours; the pressure was controlled by bleeding off the product gases (48-49).

Under steady-state pyrolysis conditions, concentrated black liquor was injected at constant flow rate into a stainless steel reactor maintained at constant temperature by an electric furnace (50). Under the batch pyrolysis conditions, product gases were drawn off and did not remain in contact with the solids for a prolonged period. During steady-state pyrolysis the pyrolyzing substrate was in constant contact with the product gases.

Comparison of steady-state pyrolysis products with those from batch pyrolysis indicates that much more gas was produced under steady-state conditions, as shown in Fig. 10. The major changes in the relative gas composition, shown in Fig. 11, were a large increase in CO and CO_2 yields.

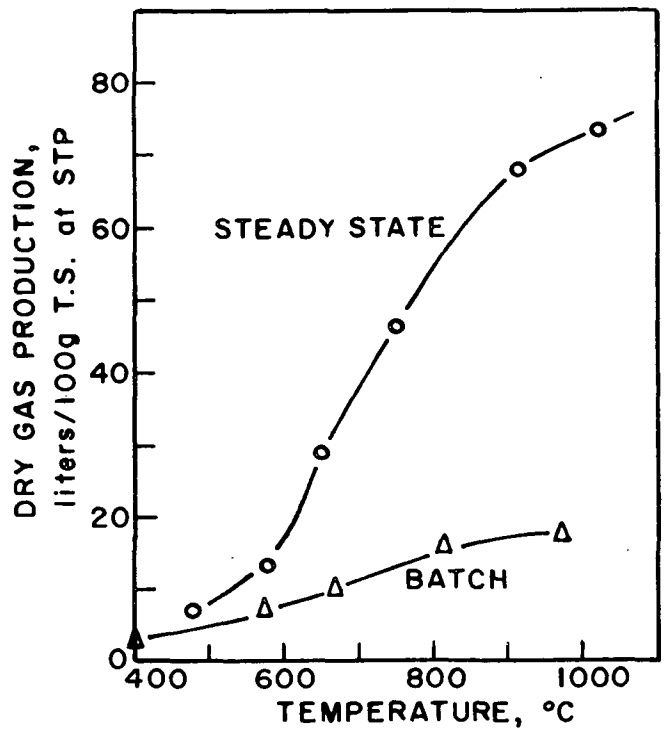


Figure 10. Volumetric gas production as a function of temperature (50).

The increased degradation under the steady-state conditions was probably due to the increased presence of steam and the catalytic effects of CO and CO_2. This phenomenon is similar to the increased degradation of wood and cellulose observed when they were pyrolyzed under the self-generated atmosphere.

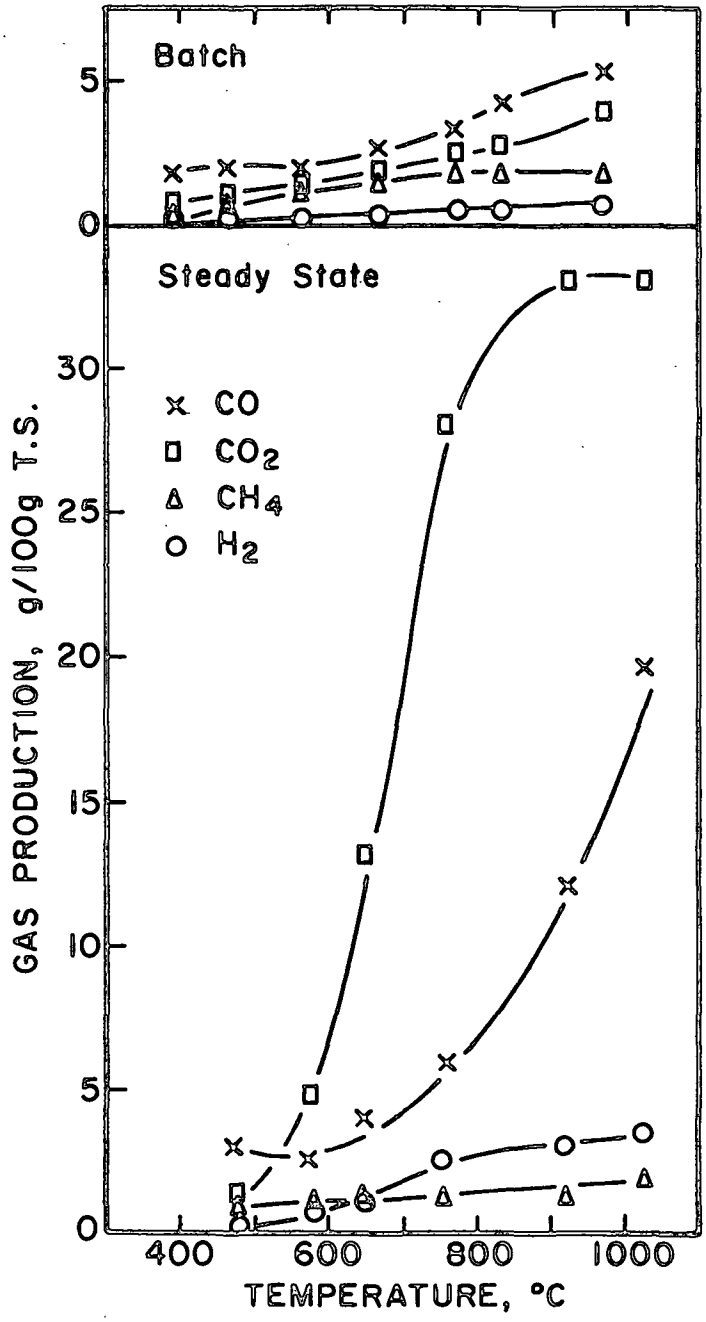


Figure 11. Weights of major gases produced as a function of temperature (50).

Another important factor influencing the pyrolysis product distribution is black liquor swelling. Heating of black liquor solids generally results in formation of a highly expanded porous structure. Fewer noncondensible noncombustible volatiles and more organic liquid (combustible volatiles) are produced during pyrolysis of swelling liquors (51). Swelling is inhibited by the presence of gallic acid or elagic

acid (51). The presence of these acids effectively "flameproofs" the black liquor by enhancing formation of char and noncombustible volatiles. The gallic acid or elagic acid, both phenolic type compounds, may inhibit the free radical decomposition leading to the formation of the lower molecular weight organic compounds necessary for swelling and the production of combustible volatiles. It has been reported (28) that certain phenolic compounds inhibit free radical reactions. At this point, however, it is not known whether the low formation of combustible volatiles is responsible for the lack of swelling or vice versa.

BLACK LIQUOR PYROLYSIS SULFUR DISTRIBUTION

During pyrolysis the sulfur present in the black liquor is distributed among the pyrolysis products (48-50). This distribution, as a function of temperature, for batch pyrolysis is shown in Fig. 12. Note that the sulfur occurs either as noncondensible volatiles or remains in the pyrolysis residue; the presence of sulfur in the condensible phases is negligible. The amount of gasified sulfur passes through a maximum near 700°C, with 70% of the sulfur in the gas phase.

The major noncondensible gases and yields are presented in Fig. 13 and 14. The production of these gases parallels that observed during wood pyrolysis, shown in Fig. 6. Increasing pyrolysis temperature affects the pyrolysis gas composition, producing relatively more combustible gases and fewer noncombustible gases such as CO_2. The distribution of gaseous sulfur compounds is of major interest here. The amount of organic sulfur compounds is many times greater than the amount of H_2S. The amount of organic sulfur gases decreases with temperature, whereas the amount of H_2S increases. This is not consistent with the behavior of sulfur during coal pyrolysis. However, the observation that volatilized sulfur is released primarily below 800°C is consistent with coal pyrolysis data.

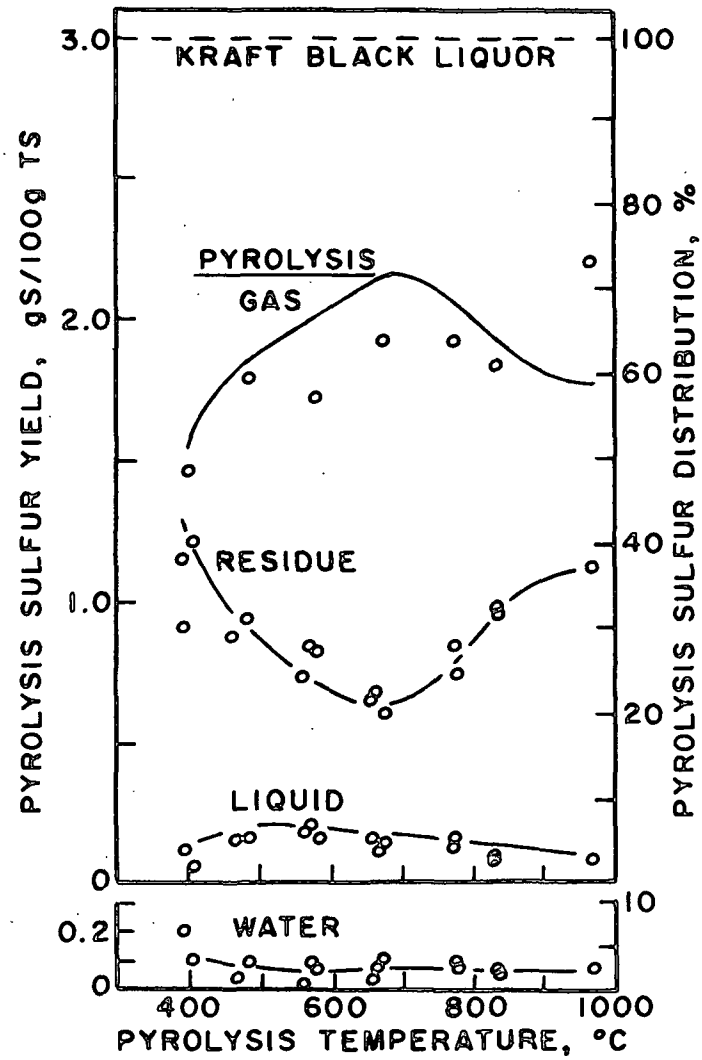


Figure 12. Sulfur distribution from batch pyrolysis (49).

It is important to note that the organic reduced sulfur compounds, methyl mercaptan, methyl sulfide, and methyl disulfide reported in Fig. 13 and 14, can originate in two ways. They may have formed during pulping (11-14) and were only stripped off during pyrolysis, or they formed during pyrolysis. The sulfur content of Feuerstein's black liquor was not characterized (48), and therefore the origin of these compounds cannot be directly determined. However, it was previously calculated that about 10% of the black liquor sulfur exists as organic sulfur compounds, suggesting that at least some of the organic compounds observed by Feuerstein were formed during pyrolysis.

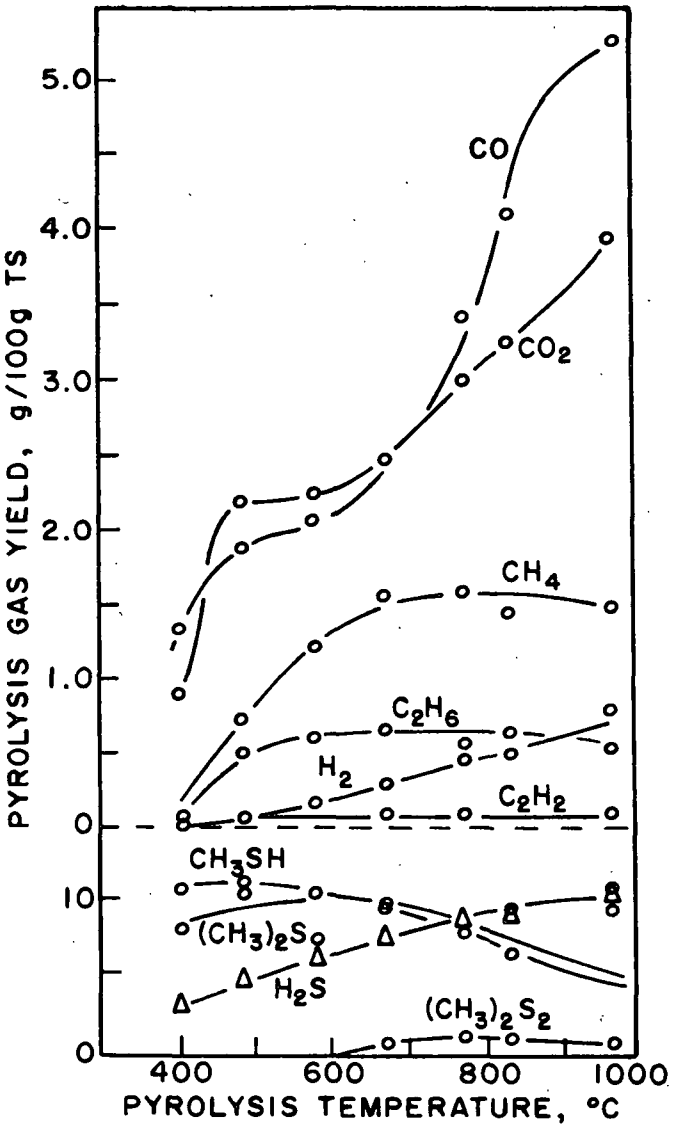


Figure 13. Individual batch pyrolysis gas yields (49).

The production of gaseous sulfur compounds is also affected by pyrolysis conditions. The results for batch pyrolysis studies have been discussed; the production of gaseous sulfur compounds under steady-state conditions is demonstrated in Fig. 15. The major effect is a maximum in H_2S production near 750°C. This maximum corresponds to about 60% of the sulfur gasified as H_2S. Of similar interest is the relatively lower ratio of organic reduced sulfur compounds to H_2S. These data indicate that the major portion of volatilized sulfur is released below about 800°C.

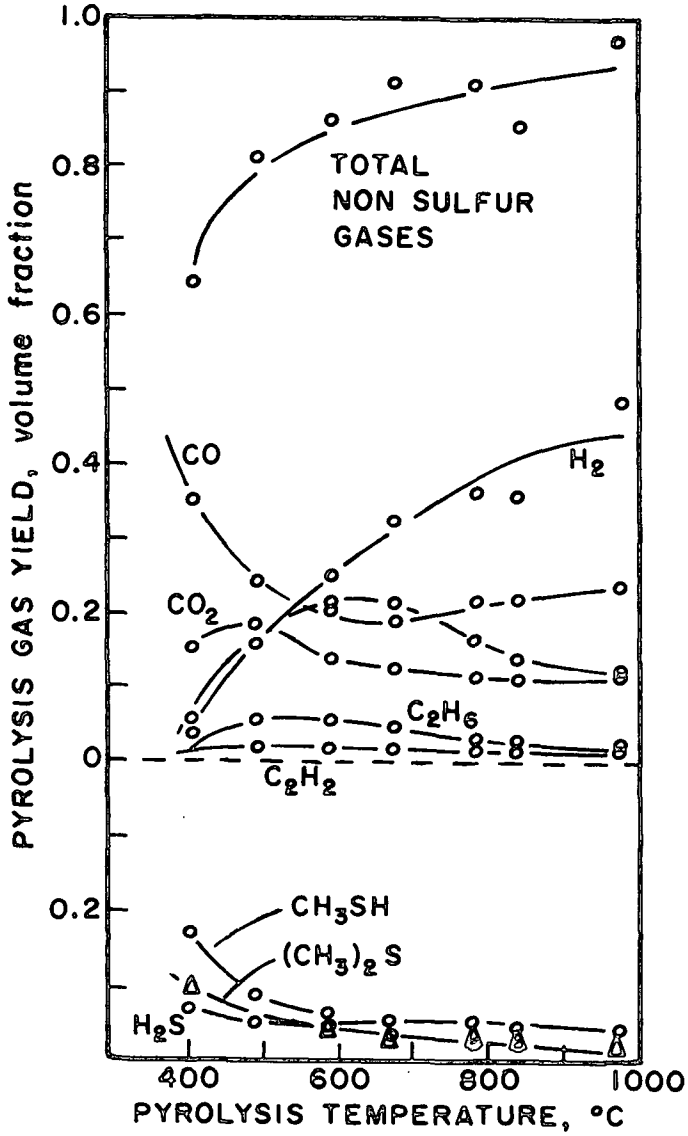


Figure 14. Batch pyrolysis gas yields (49), volume basis.

In the preceding studies the form of sulfur in the black liquor was unknown. It was later found by Douglass and Price (52) that the chemical form of the sulfur is also an important factor affecting the pyrolysis sulfur distribution. Several pyrolyses of inorganic sulfur compounds with one of two organic compounds were carried out at 600°C with a nitrogen purge. The gas stream was bubbled through an acidified solution of cadmium chloride designed only to remove H_2S and not mercaptans. The results are presented in Table V.

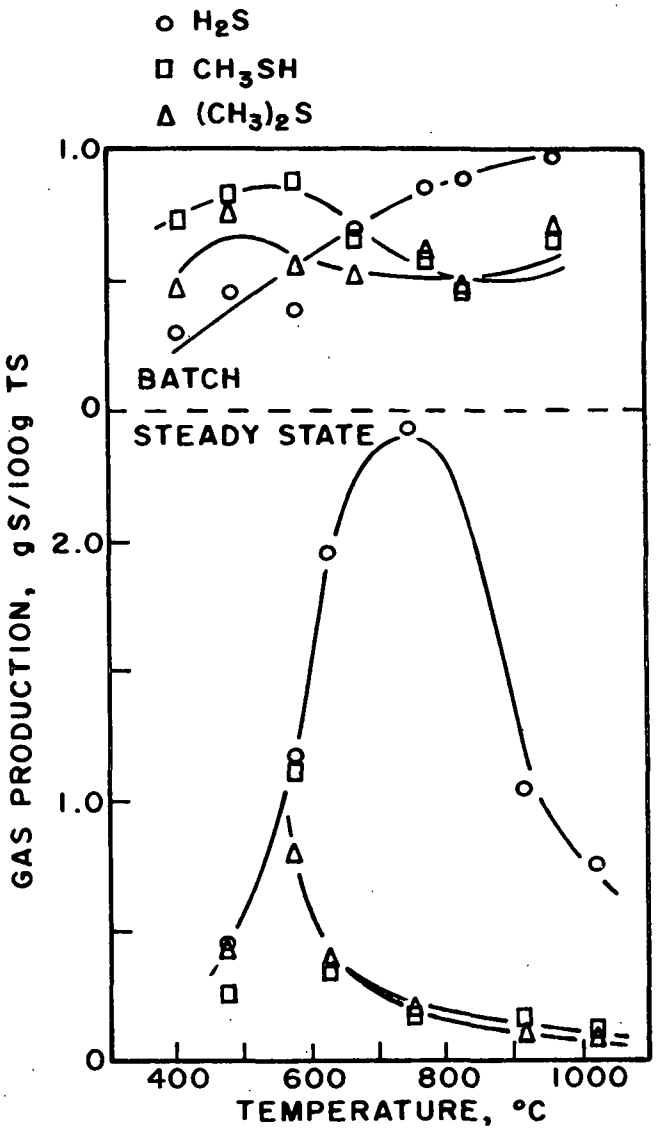


Figure 15. Weights of major sulfur gases produced as a function of temperature for batch and steady-state pyrolysis (50).

The data in Table V indicate that the largest production of H_2S occurs from the pyrolysis of $Na_2S_2O_3$, Na_2S, or elemental sulfur with either organic material. Extrapolating from these data to a black liquor composed of equal amounts of lignin and glucose with either $Na_2S_2O_3$ or Na_2S (elemental sulfur is not reported to be present in black liquor) indicates that about 50% to 60% of the sulfur is expected to be gasified as H_2S. Calculations from Fig. 13 indicate that about 67% of the

total black liquor sulfur is gasified at 600°C, and is equally distributed among H_2S, CH_3SH, and $(CH_3)_2S$. The much higher yield of H_2S and consequent lower yields of organic sulfur, observed by Douglass and Price starting with known inorganic sulfur sources, is not consistent with the amount of organic sulfur gases found by Feuerstein.

TABLE V

HYDROGEN SULFIDE FORMED IN HEATING ORGANIC MATERIALS WITH SULFUR AND SULFUR COMPOUNDS AT 600°C (52)

(In Millimoles of Hydrogen Sulfide Produced)

	Sulfur Compound, 1.0 mmole of each used					
Organic Material	Blank	Na_2SO_4	Na_2SO_2	$Na_2S_2O_2$	Na_2S	S
Soda lignin	0.004	0.004	0.015	0.786 0.736	0.370	0.750
Glucose	0.004	0.004	0.064	1.456 1.523 1.500 1.517	0.605	0.348
Theoretical maximum	0.0	1.00	1.00	2.00	1.00	1.00

The organic reduced sulfur compounds can originate in two ways, as mentioned earlier. They can form during pulping and be stripped off during pyrolysis or they can form during pyrolysis. If the trends observed by Feuerstein really existed, it would indicate that his organic reduced sulfur compounds were probably originating during pyrolysis. However, the tabulated data present in Feuerstein's thesis (48) illustrate poor reproducibility of gas analysis data for duplicate pyrolyses; the trends shown in Fig. 12, 13, and 14 are approximate and possibly misleading. Therefore, Feuerstein's observed organic sulfur compounds probably originated in the liquor. This is supported by two other factors. First, Feuerstein's pyrolyses were done sequentially in time, so pyrolysis at higher temperatures generally corresponded to pyrolysis of an older liquor sample. The sulfur compounds present in black liquor readily oxidize (14) so that some oxidation is expected

during liquor storage. The methyl disulfide observed in the later pyrolyses at higher temperatures is the oxidation product of methyl mercaptan (14) and could be due to liquor aging instead of pyrolysis. Second, the sum of sulfur present as methyl mercaptan, methyl sulfide, and methyl disulfide, calculated from Feuerstein's tabulated data, is fairly constant; this would be expected if these compounds were initially present in the liquor. These considerations suggest that a large amount of organic sulfur compounds was present in Feuerstein's black liquor, more than the previously calculated 10%.

Another interesting aspect of Douglass and Price's data is the similarity in the sulfide and thiosulfate pyrolysis results. The proportions of sulfur that appear as H_2S from thiosulfate or sulfide were about the same during pyrolysis with either organic. This could be due to similar reaction mechanisms or to experimental problems.

The black liquor pyrolysis sulfur distribution displays differences from and similarities to the coal sulfur distribution. The principal similarity is the observation that volatile sulfur is released below 800°C. However, the volatile sulfur compounds formed during pyrolysis below 800°C are different for both materials. The principal sulfur gas product from coal pyrolysis is H_2S. During black liquor pyrolysis Feuerstein observed a mixture of organic reduced sulfur gases. It is not certain, however, whether these compounds were formed during pyrolysis or were initially present in the black liquor.

The selection of a mechanism or mechanisms from the many possible reactions leading to sulfur volatilization depends on knowing both starting materials and products. This information is not available in the recorded literature. Feuerstein did not know the starting state of the black liquor sulfur. Douglass and Price only determined one gaseous sulfur product from known starting materials. Neither determined

the state of sulfur in the solid residue. Therefore, it is impossible to determine any mechanisms.

In summary, black liquor pyrolysis begins after the liquor has dried and is usually accompanied by swelling. The pyrolysis products include noncondensible volatiles, an aqueous distillate, an organic tar, and a carbonaceous char containing sodium salts. The black liquor sulfur is primarily distributed between the noncondensible volatiles and the char. The sulfur distribution is affected by the pyrolysis conditions, the organic materials, and the initial forms of sulfur. Sulfate was observed to be inert. Sulfite, sulfide, and thiosulfate all produced some H_2S during pyrolysis with soda lignin or glucose. Douglass and Price found that pyrolysis of sulfide and thiosulfate gave similar results. Most of the volatilized sulfur is released below 800°C. There is some controversy over the principal gaseous sulfur products formed during pyrolysis. Complete information on sulfur products starting from well-defined sulfur compounds is needed.

THERMODYNAMICS

Chemical thermodynamics can be invoked to explain much of the previously presented black liquor pyrolysis behavior. Thermodynamic study involves the determination of the equilibrium composition of the system under investigation. To determine the equilibrium composition only the elemental analysis of the system is important; the initial state of the compounds is not needed. Equilibrium calculations assume that the starting material is completely converted to the thermodynamically favored products at the particular temperature and pressure. Several techniques have been applied to calculating the equilibrium composition for combustion of sodium-based liquors (53-56).

The approach of Bauers and Dorland (56) was to simultaneously solve equilibrium expressions involving all the species considered present. Solutions were obtained

by making the equilibrium oxygen partial pressure an independent variable. The stoichiometric constraints were satisfied by fixing relationships between a limited number of variables:

$$P_{CO_2} + P_{CO} = 0.15 \text{ atm.}$$

$$P_{H_2O} + P_{H_2} = 0.15 \text{ atm.}$$

$$P_{H_2S} + P_{SO_2} + P_{SO_3} + \frac{1}{2} P_{S_2} \leq 0.01 \text{ atm.}$$

P = partial pressure.

The results of the calculations pertaining to the pyrolysis sulfur distribution are shown in Fig. 16. The ordinate 'Δ' is the approximate oxygen excess (or deficiency) and is defined (56):

$$\frac{\Delta\ \%}{100} = P_{O_2} - \frac{1}{2} P_{H_2} - \frac{1}{2} P_{CO}$$

During pyrolysis more reduced compounds are formed than during combustion, for which the equation was defined. Therefore 'Δ' can only be regarded, at this point, as an upper limit; the oxygen deficiency will be greater (a smaller oxygen excess).

The labeled regions of Fig. 16 bordered by solid lines indicate those regions of the plane which correspond to more than 99% of the total sulfur existing as that compound. For example, at an oxygen excess of zero or more, $\Delta > 0$, the major sulfur product is Na_2SO_4. Within the unlabeled area the sulfur is distributed in varying proportions between the solid and gaseous phases.

The oxygen deficiency '$-\Delta$' can be calculated from the volume fractions of pyrolysis product gases shown in Fig. 14, with the partial pressure of oxygen equal to zero.

$$-\Delta\ \%_{400°C} = 20\%$$

$$-\Delta\ \%600°C = 29\%$$

$$-\Delta\ \%_{800^\circ C} = 29\%$$

$$-\Delta\ \%_{1000^\circ C} = 30\%$$

The curve in Fig. 16 (when applied to Feuerstein's data, using the values of 'Δ' calculated above) indicates that H_2S is not expected above 500°C. This does not agree with Feuerstein's results.

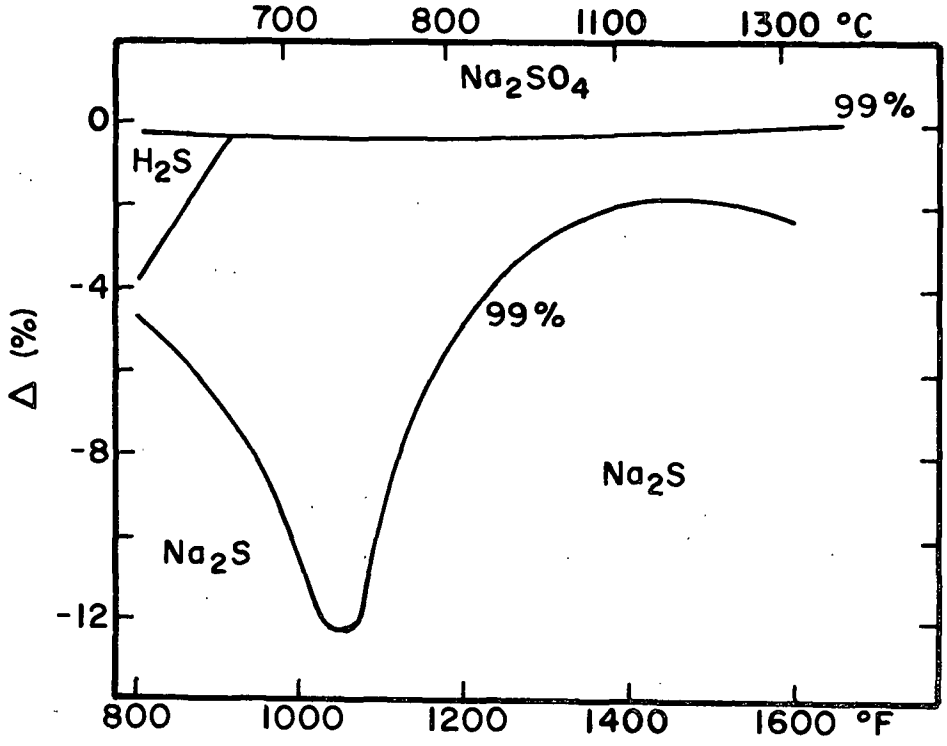


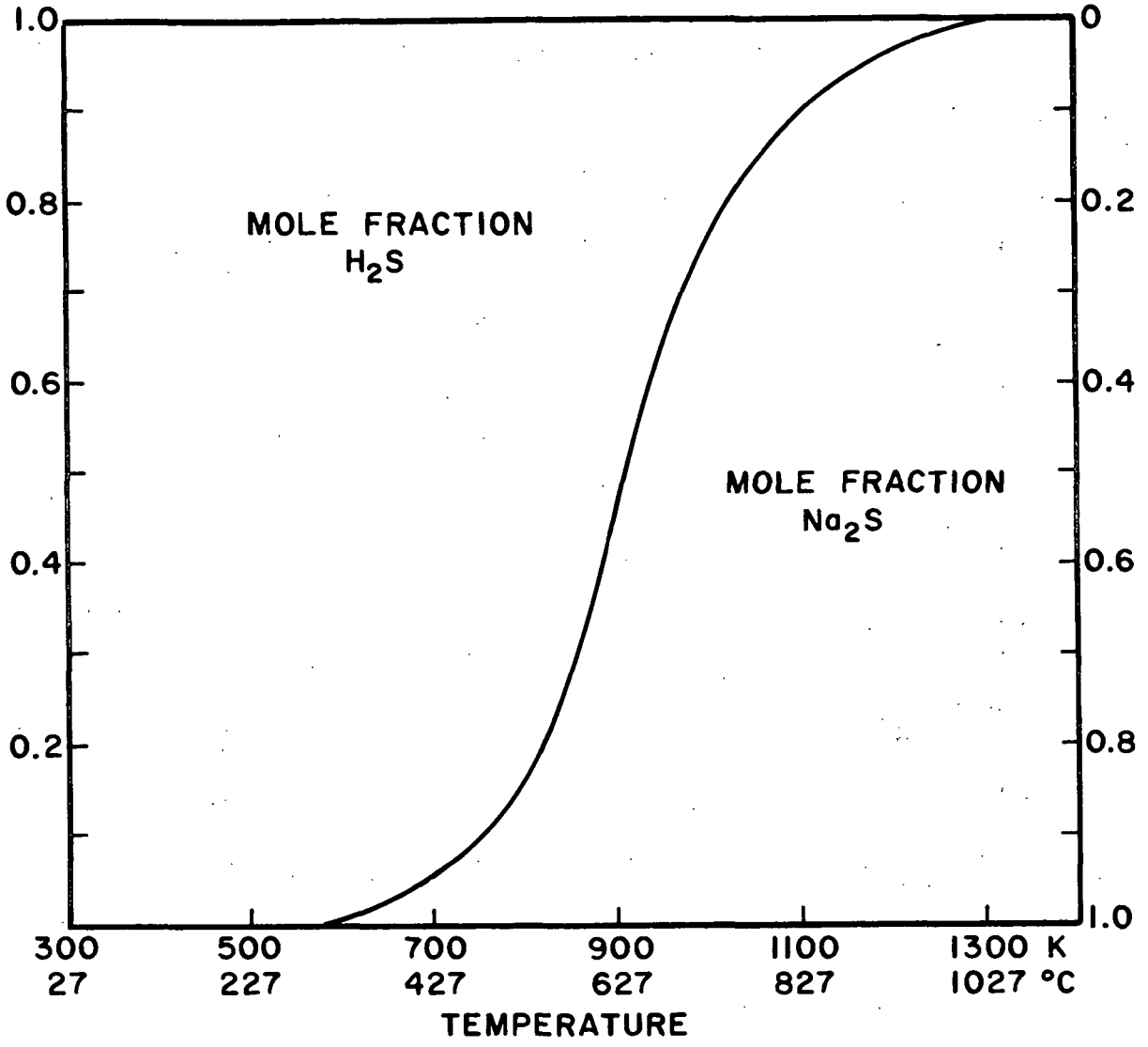
Figure 16. Stoichiometric diagram (56).

Figure 16 cannot be used for temperatures lower than 500°C. An idea of the sulfur distribution below 500°C can be obtained by looking at the reaction:

$$Na_2S(s) + CO_2(g) + H_2O(g) \rightarrow Na_2CO_3(g) + H_2S(g)$$

The thermodynamic sulfur distribution for this reaction is plotted in Fig. 17. Equilibrium constants were calculated from the JANAF (57) thermodynamic tables.

Figure 17 indicates that below 300°C the principal sulfur product is H_2S. As the temperature increases, Na_2S becomes more favored. Therefore, under low-temperature pyrolysis conditions, thermodynamics predicts total volatilization of the sulfur if CO_2 and H_2O are present.



$$Na_2CO_3 + H_2S \rightleftharpoons Na_2S + CO_2 + H_2O$$

Figure 17. Thermodynamic sulfur distribution.

COMPARISON OF BLACK LIQUOR PYROLYSIS RESULTS WITH THERMODYNAMIC PREDICTIONS - AN ANALYSIS

Experimental pyrolysis results, shown in Fig. 12 and 15, indicate that an increase in H_2S production was obtained with an increase in pyrolysis temperature up

to between 700°C and 750°C. This is in contradiction to thermodynamic prediction. Thermodynamics indicates almost total volatilization of sulfur below 300°C, followed by the amount of Na_2S increasing with temperature. Apparently, the reactions leading to the release of volatile sulfur compounds are very slow and, therefore, a rate-controlling factor. As the temperature rises, the reactions become faster and more volatile sulfur is released.

Above 750°C thermodynamics predicts that under pyrolysis conditions all the sulfur should be present in the solid phase as Na_2S (see Fig. 16). Although all the sulfur was not observed in the solid phase in the pyrolysis studies previously discussed, it was approached to varying degrees. The increase of solid phase sulfur with temperature during steady-state pyrolysis above 750°C, inferred from Fig. 15, is greater than that observed during batch pyrolysis, Fig. 12. This is probably due to the bleeding off of product gases during Feuerstein's batch pyrolyses with the consequent inability for a back-reaction between the sulfur gases and the solid phase to take place. Under steady-state pyrolysis conditions where the product gases remain in contact with the solids at the high temperatures, a reaction between the sulfur gases and solid can readily take place.

At similar high temperatures during coal pyrolysis it was observed that the gaseous sulfur compounds can re-react with the basic minerals present in the coal. This reaction is very fast. Since black liquor contains basic sodium carbonate, a similar back-reaction is possible. The back-reaction is:

$$Na_2CO_3(s) + H_2S(g) \rightarrow Na_2S(s) + H_2O(g) + CO_2(g)$$

The thermodynamic sulfur distribution for this back-reaction is depicted in Fig. 17. The back-reaction becomes thermodynamically favored above about 650°C.

The rate of this back-reaction has been studied (58) and is reported to be very fast. This fast back-reaction allows a rapid approach to thermodynamic equilibrium

at the high pyrolysis temperature. This accounts for the large increase in solid phase sulfur under steady-state pyrolysis. It is concluded that the pyrolysis sulfur distribution is kinetically controlled at low temperatures and approaches thermodynamic control above 750°C.

SULFUR VOLATILIZATION REACTIONS AND KINETICS

Since the low-temperature pyrolysis sulfur distribution is kinetically controlled, it is important to consider reaction mechanisms. Presently, the mechanisms leading to sulfur volatilization are unknown. However, the literature does contain information on reactions which may be taking place.

The sulfur gases that may form during pyrolysis include H_2S, CH_3SH, $(CH_3)_2S$, $(CH_3)_2S_2$, COS, and SO_2. The formation of all these compounds, with the possible exception of SO_2, must involve the decomposition of an organic material. The work of Douglass and Price suggests that volatile sulfur is released principally from sulfide or thiosulfate during pyrolysis.

Sodium sulfide is very hygroscopic and generally exists as a hydrate. Thermal analysis of $Na_2S \cdot 9H_2O$ under a mixture of nitrogen (90%) and hydrogen (10%) indicates that during heating only water vapor is removed; negligible amounts of H_2S are reported (66). The water of hydration is not totally removed until above 830°C. The hydrates are very reactive toward carbon dioxide, forming Na_2CO_3 and H_2S (59).

Sodium thiosulfate thermally decomposes to sodium sulfate and sodium polysulfide (60-63):

$$4\ Na_2S_2O_3 \xrightarrow[\Delta]{} +\ 3\ Na_2SO_4 + Na_2S_5$$

At 250°C the half-life for the decomposition is 1.5×10^6 hours; at 350°C the half-life is 11.4 hours, decreasing to 7.9 seconds at 450°C. The half-lives were calculated from rate constants presented in reference (63).

The early low-temperature organic pyrolysis products are noncombustible volatiles consisting of CO_2, water vapor, and organic acids. These products may react directly with Na_2S or $Na_2S_2O_3$ to form H_2S, the principal sulfur gas observed by Douglass and Price. Some relevant reactions are in Table VI.

TABLE VI

DIRECT SULFUR VOLATILIZATION REACTIONS[a]

	Δ H	Δ G
$Na_2S + H_2O + CO_2 \rightleftharpoons Na_2CO_3 + H_2S$	-34.1	-132.04
$Na_2S + 2CO_2 \rightleftharpoons Na_2CO_3 + COS$	-26.08	-14.57
$Na_2S + 2HCO_2H \rightleftharpoons Na_2CO_3 + H_2S + CH_2O$	-40.28	-37.47
$Na_2S_2O_3 + H_2O \rightleftharpoons Na_2SO_4 + H_2S$	-10.1	-22.77
$Na_2S_2O_3 + CO_2 \rightleftharpoons Na_2SO_4 + COS$	-2.1	-14.57
$Na_2S_2O_3 + CO \rightleftharpoons Na_2SO_3 + COS$	-0.26	-12.72

Δ H, Δ G = kcal/mole

[a]Calculated from (57).

Interactions with acidic organic pyrolysis products may also cause sodium thiosulfate to decompose by another mechanism. At low temperatures in the presence of even weak acids such as carbonic acid, thiosulfate decomposes to sulfur dioxide and elemental sulfur (60,61,64). The overall reaction is:

$$2\ H^+ + S_2O_3^{=} \rightarrow H_2O + SO_2 + S^o$$

This reaction typically takes place in solution but could possibly take place as a heterogeneous reaction between solid thiosulfate and a gaseous organic acid. Examples of such a reaction that might occur during pyrolysis are:

$$Na_2S_2O_3 + 2\ HCO_2H \rightarrow 2\ NaHCO_3 + SO_2 + S^o + H_2O$$

$$Na_2S_2O_3 + CO_2 \rightarrow Na_2CO_3 + SO_2 + S^o$$

The later forming higher temperature organic pyrolysis products are usually combustible volatiles such as H_2, CH_4, and CO. These compounds could reduce thiosulfate. Thiosulfate is observed to be reduced by reaction with some organics (61). An example of such a reaction is:

$$Na_2S_2O_3 + 3CO \longrightarrow Na_2S + S^o + 3CO_2$$

$$\Delta H = -25.1 \text{ kcal/mole}$$

$$\Delta G = -28.0 \text{ kcal/mole}$$

Polysulfide reacts similarly to elemental sulfur in many reactions (61). They are both relatively strong oxidants which can abstract hydrogen from organic materials to form H_2S or combine to form organic sulfur compounds. The amount of organic sulfur increases during coal pyrolysis (35). These reaction mechanisms are not well understood (61). Polysulfur or elemental sulfur can also be reduced and remain in the solid phase as Na_2S.

Carbonyl sulfide (COS), observed in recovery stack gases (65), is a possible reaction intermediate which can lead to H_2S or other organic sulfur compounds (66). H_2S is formed by hydrolysis of COS:

$$COS(g) + H_2O(g) \rightleftharpoons H_2S(g) + CO_2(g)$$

$$\Delta H = -7.99 \text{ kcal/mole}$$

$$\Delta G = -8.20 \text{ kcal/mole}$$

Under low-temperature pyrolysis conditions H_2S is the thermodynamically favored product. If COS is formed directly by one of the reactions listed in Table VI, it is expected to hydrolyze to H_2S. However, the hydrolysis reaction is very slow unless catalyzed (65). One catalyst that is present during pyrolysis of black

liquors is Na_2CO_3. Table VII compares the rate constants for the uncatalyzed and Na_2CO_3-catalyzed hydrolysis reactions of COS.

TABLE VII

RATE CONSTANTS FOR THE UNCATALYZED AND THE SODIUM CARBONATE-CATALYZED GAS-PHASE HYDROLYSIS OF COS BETWEEN 100 and 200°C (65)

Temperature, °C	Catalyzed[a] $k_{COS} \times 10^3$ sec^{-1}	Uncatalyzed[b] $k_{COS} \times 10^6$ sec^{-1}
102 (± 10)	0.72	0.8
142 (± 10)	3.50	2
158 (± 10)	13.80	5
175 (± 15)	22.50	20
200 (± 15)	33.40	500

The half-life for the 102°C uncatalyzed reaction is 241 hours; for the catalyzed reaction it is 16 minutes. At 200°C the half-life for the uncatalyzed reaction is 23 minutes; for the catalyzed reaction, 21 seconds. At somewhat more elevated temperatures COS may be an important reaction intermediate during black liquor pyrolysis, quickly hydrolyzing to H_2S.

The data of Douglass and Price, Table V, indicate that sulfite and sulfate produce little H_2S. More H_2S is formed, however, during pyrolysis of Na_2SO_3 with glucose than with the alkali lignin. Sodium sulfate is reported to be inert and forms no H_2S during pyrolysis. Reactions of these salts are therefore not discussed.

ANALYSIS

Knowledge of the reactions leading to the formation of gaseous sulfur compounds would increase understanding of the sulfur cycle within the recovery furnace and lead to increased ability to control furnace processes. Determination of the sulfur volatilization reactions has not been an objective of any reported black liquor

pyrolysis study. The studies of Douglass and Price (52), Feuerstein (48-49), and Brink (50) were primarily concerned with how much reduced sulfur gases were formed during pyrolysis. The work of Prahacs, Gaval, and Barclay (53-54) dealt with pyrolysis of spent sulfite liquors; any mechanisms, even if determined, would not have been pertinent to this study.

Determination of the sulfur volatilization reaction mechanisms demands knowledge of both starting materials and products. Among the investigations previously discussed, only Douglass and Price started with sulfur in an initially known state. However, they were only interested in the amount of H_2S produced and did not determine what other sulfur gases may have been produced.

Feuerstein identified most of the gaseous sulfur pyrolysis products but did not know the initial sulfur forms; it is possible that much of the organic reduced sulfur compounds observed during his pyrolyses was present in the starting liquor. Neither Douglass and Price nor Feuerstein identified the forms of sulfur remaining in the solid residue.

Information necessary to determine the reaction mechanisms should be obtainable by determining all the sulfur pyrolysis products starting with a well-defined system. Since black liquor is a very complex ill-defined system it is necessary to work with a less complex system. This can be accomplished by pyrolyzing mixtures of simple organic materials, representative of those found in black liquor, and inorganic sulfur salts. The inorganic sulfur salts of most interest include Na_2S, $Na_2S_2O_3$, Na_2SO_3, and Na_2SO_4.

To investigate the reactions it is necessary to avoid thermodynamically controlled behavior. The literature reports that the back-reaction of H_2S with Na_2CO_3 becomes thermodynamically favored above 650°C. This reaction is also reported to become fast at somewhat higher temperatures. This indicates that pyrolyses should be

carried out below 650°C to maintain kinetically controlled behavior during sulfur volatilization.

The thermal stability of hydrated sodium sulfide indicates that during pyrolysis, anhydrous sulfide could retain captured organic pyrolysis water to a high temperature. This hydrated sulfide would readily react with carbon dioxide to form Na_2CO_3 and H_2S by the following reaction:

$$Na_2S + H_2O + CO_2 \rightleftharpoons Na_2CO_3 + H_2S$$

If hydrogen sulfide is stripped by a reaction similar to that described above during pyrolysis, it is expected that the sulfur form remaining in the char should be primarily sodium sulfide.

If thiosulfate is reduced to sulfide prior to sulfur volatilization, then the pyrolysis gases and char sulfur forms should be similar to those obtained from sulfide pyrolysis. The results of Douglass and Price, Table V, indicate that the same proportion of sulfur was volatilized as hydrogen sulfide during pyrolysis of sulfide as during pyrolysis of thiosulfate with both glucose and soda lignin. This suggests similar reaction mechanisms.

During the later stages of the organic pyrolysis, when the major products are combustible volatiles (reducing agents), thiosulfate could be reduced to sulfide and elemental sulfur. However, this sulfide and elemental sulfur are not expected to be readily volatilized. The CO_2 and H_2O necessary for H_2S stripping are not available because of their much earlier release.

Thiosulfate can also react to produce sulfur gases by either direct reaction with organic pyrolysis products or by an intermediate decomposition to sulfur dioxide and elemental sulfur. Direct reaction of sodium thiosulfate with CO_2 or H_2O will leave large amounts of sulfate or sulfite in the solid residue (Table VI).

Acid decomposition would drive off SO_2 and leave elemental sulfur which could react further. The elemental sulfur formed by decomposition or reduction of thiosulfate is a good oxidant which could be reduced to form volatile sulfur compounds or solid phase sulfur compounds such as residual organic sulfur or Na_2S.

Any thiosulfate remaining after the organic is totally decomposed will thermally decompose to sulfate and polysulfide.

If COS is an important reaction intermediate, the catalyzed hydrolysis reaction may mask it. Thermodynamics indicates that at low temperatures the desired product of the hydrolysis reaction is H_2S which readily forms in the presence of sodium carbonate, a catalyst present during black liquor pyrolysis. The masking of a COS intermediate by the rapid hydrolysis reaction can be minimized as a problem by use of a batch flow-through reactor from which the pyrolysis product gases are continuously removed and therefore do not remain in contact with the pyrolysis solids.

THESIS OBJECTIVES

The objectives of this thesis study were to investigate the reactions leading to volatilization of inorganic sulfur during black liquor pyrolysis. Specifically, this study was to determine how sodium sulfide, sodium thiosulfate, sodium sulfite, and sodium sulfate reacted under pyrolysis conditions in the presence of sodium gluconate or vanillic acid. The questions to be answered were:

- Which compounds lead to substantial amounts of volatile sulfur?
- Does sulfate react at all under pyrolysis conditions?
- What are the important variables affecting the pyrolysis sulfur distribution?

The second objective of this study was to relate the pyrolysis behaviors of sulfur salts which lead to large amounts of volatile sulfur to known reactions of the salts. This would provide the basis from which to postulate the reaction mechanisms leading to volatilization of inorganic sulfur.

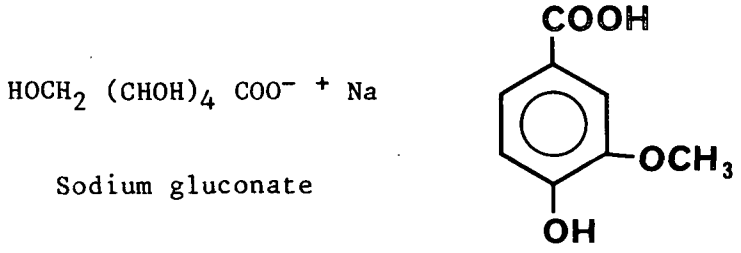
A third objective was to relate the results to the literature. What was of specific concern was whether or not the results of Douglass and Price, which suggested similar pyrolysis behavior for sulfide and thiosulfate, were valid.

EXPERIMENTAL

Pyrolysis product information was obtained in the following manner. Pyrolytic degradations of mixtures consisting of a well-defined organic compound and inorganic sulfur source were carried out at constant heating rates. The pyrolysis gas was analyzed for the amounts and types of sulfur-containing gases. The pyrolysis residue was analyzed for the remaining sulfur forms.

MATERIALS

The compounds selected as organic components were sodium gluconate and vanillic acid. The sodium gluconate is similar to the hydroxy acid sodium salts found in black liquor. Vanillic acid is representative of the alkali lignin degradation products and is reported to be present in black liquors (9). The inorganic sulfur sources were Na_2S, $Na_2S_2O_3$, Na_2SO_3, and Na_2SO_4.



Sodium gluconate

Vanillic acid

The sodium gluconate was dried, ground, and screened to 45-100 mesh for pyrolysis. The vanillic acid could not be ground or screened and was used as received. The inorganics were dried, ground, and screened to two mesh sizes; 28-45 mesh and 45-100 mesh. All materials except Na_2S were dried at 105°C and stored in a vacuum desiccator over P_2O_5. Sodium sulfide was ground and screened to the desired mesh size ranges and then stored over P_2O_5 under vacuum. Sodium sulfide was analyzed prior to each pyrolysis.

PYROLYSIS

All pyrolyses were carried out with dry samples. Two and one-half grams of organic material was used in each pyrolysis, with enough of the inorganic sulfur salt

to provide 0.2 gram sulfur. Initial trials were replicated. Since the reproducibility was good, latter trials were not duplicated.

The sample to be pyrolyzed was weighed into a high-density alumina high-top crucible from Coors Porcelain Company, Golden, Colorado. Regular porcelain crucibles reacted visibly under pyrolysis conditions. The crucible with sample was then placed into a crucible holder which slid into the three-inch O.D. 316L stainless steel reactor. The reactor was heated in a tubular muffle furnace.

During pyrolysis a nitrogen purge was maintained. The flow rate was adjusted and monitored with an orifice meter. The purge gas passed through the reactor and out of the furnace, through a condenser, and was collected in 44-liter laminated aluminum-polyester bags from Alltech Associates. The bags were removed and replaced every 20 minutes during pyrolysis; gas analysis by gas chromatography was carried out immediately after bag removal.

Two different heating rates were obtained in the following ways. A low rate of 13°C per minute could be obtained by placing the reactor into the cool furnace and then switching on the power. A higher heating rate of 23°C per minute was obtained by quickly placing the reactor into the furnace preheated to 550°C.

After pyrolysis the reactor was removed from the furnace and allowed to cool while the nitrogen purge continued. When cool, the reactor was opened and the crucible was removed and transferred to a vacuum desiccator with P_2O_5 desiccant. All further char manipulations, such as grinding and transfers, were done under nitrogen in a glove bag.

The polysulfide, sulfite, and thiosulfate analyses were done immediately after pyrolysis. The solid sample for sulfate analysis was placed in concentrated HCl and evaporated to dryness (see Appendix II) prior to storage. The solids for sulfide

analysis were placed in a sulfide antioxidant buffer (SAOB II) solution for storage. The solids for the total sulfur analysis were treated with 5 milliliters of a 30% H_2O_2 solution prior to storage. The full analytical procedure is given in Appendix I.

The variables investigated were:

1) Composition
2) Heating rate
3) Particle size of inorganic salt
4) Nitrogen purge rate

The fully tabulated results are in Appendix II.

RESULTS AND DISCUSSION

SULFUR BALANCE CLOSURE

Eighty pyrolyses were run. The early trials were used to identify the important variables affecting the sulfur volatilization. When these variables had been identified, pyrolyses were run to gather the information necessary to determine the sulfur volatilization reactions.

The mean sulfur closure for the latter pyrolyses, Pyrolyses 44 to 76, was 98.0%, with a coefficient of variation of 12.2%. The closure calculated for Feuerstein's pyrolyses (48) averaged 96%, with a coefficient of variation of 10%.

Sulfur balance variation in this study and Feuerstein's study was due primarily to variations in the gas analysis. This study revealed that sulfur closure was affected by the nitrogen purge rate and gas sampling time. Complications due to these effects could be minimized and sulfur balance closure maintained by analyzing the pyrolysis gases immediately after the gas bags were removed from the system. The specific effect of nitrogen purge rate is discussed in a later section.

REPRODUCIBILITY

Pyrolyses of sodium thiosulfate with sodium gluconate were used to determine the reproducibility of the pyrolysis trials. The pyrolysis of sodium thiosulfate with sodium gluconate was the most complex pyrolysis studied and gave the most difficulty with analysis. The results of four pyrolyses are given in Table VIII. The amount of sulfur remaining in the solid residue was very reproducible, with less than a 2% coefficient of variation. The total amount of sulfur in the gas phase, calculated as the sum of the individual components, was less reproducible, with a coefficient of variation of 33.5%.

TABLE VIII

REPLICATES OF SODIUM THIOSULFATE AND SODIUM GLUCONATE PYROLYSIS, HEATING RATE 13°C/MINUTE, 45-100 MESH $Na_2S_2O_3$ (EXPRESSED AS PERCENT OF INITIAL SULFUR)

Solid Residue Sulfur Analysis	Pyrolysis 38	39	52	54	mean	s.d.
$S^=$	40.9	42.5	39.6	37.9	40.2	2.0
S_x	12.6	13.1	10.9	13.0	12.4	1.0
$S_2O_3^=$	0.0	0.0	0.0	0.0	0.0	0.0
SO_3	0.9	1.3	2.6	1.6	1.6	0.6
SO_4	2.2	4.8	4.6	4.7	4.1	1.3
Total sulfur	70.0	69.1	71.7	68.7	69.9	1.3
Gas Analysis						
H_2S	9.2	8.0	17.1	11.9	11.6	4.0
COS	0.4	0.5	0.6	0.6	0.5	0.1
SO_2	1.4	3.1	3.6	1.9	2.5	1.0
CH_3SH	0.2	0.4	1.0	0.9	0.6	0.4
Other	0.4	0.5	0.9	0.6	0.6	0.2
Total sulfur recovery	81.6	81.6	95.5	85.3	86.0	6.6

Though the amount of sulfur that could be accounted for in the gas phase was less reproducible than in the solid phase, Table IX indicates that the relative composition of the pyrolysis gas was very constant. This was also seen for pyrolyses under different conditions and was not a unique observation. Therefore, the amount of sulfur volatilized was best determined as the difference between the initial sulfur and the total sulfur in the solid residue. The relative gas composition was determined from the gas analysis. The overall reproducibility was then very good. This is discussed in Appendix II.

TABLE IX

RELATIVE GAS COMPOSITION

Pyrolysis I.D. Number	40	44
Total Sulfur Gas	6.32%	10.26%
Percentage of Total as:		
H_2S	65.5	65.9
COS	4.9	5.8
SO_2	22.2	21.1
CH_3SH	3.3	2.9
Other	4.1	4.4
	100.0	100.0

THERMAL CHARACTERIZATION OF PYROLYSIS MATERIALS

It is known that the formation of gaseous sulfur compounds during pyrolysis must be linked to the pyrolysis behavior of the organic compound. However, as suggested by the cellulose flameproofing studies, the presence of the inorganic material would be expected to influence the pyrolysis behavior of the organic compound.

Thermogravimetric analyses (TGA) of the organic materials with and without sodium thiosulfate were carried out at Polytechnic, Inc., Lincolnwood, Illinois. The TGA's were carried out from 30°C to 370°C, with a heating rate of 10°C per minute and a nitrogen purge rate of 10 cc per minute. Vanillic acid decomposed between 150°C and 300°C, with a maximum weight loss rate near 240°C. In the presence of thiosulfate the vanillic acid TGA curve was very different, showing reaction between 140°C and 230°C, with a maximum weight loss rate near 220°C. The sodium gluconate decomposed between 210°C and 270°C, with a maximum decomposition rate at 227°C.

When thiosulfate was present the sodium gluconate reacted between 200°C and 280°C, with a maximum weight loss rate at 222°C.

Analyses, described in Appendix I, to determine the amounts of volatiles and nonvolatiles formed during pyrolysis of the organic starting materials were performed alone and in the presence of sodium thiosulfate. The results of the analyses are shown in Table X. More volatiles formed during pyrolysis of the vanillic acid than during pyrolysis of the sodium gluconate. The presence of the thiosulfate increased the amount of volatiles formed during vanillic acid pyrolysis. The presence of thiosulfate did not appear to affect the volatilization of sodium gluconate. A mixture of the two organic compounds gave nonadditive effects; more material was volatilized than was predicted from the pyrolyses of the individual compounds.

TABLE X

DETERMINATION OF THE VOLATILE AND NONVOLATILE FRACTIONS OF THE ORGANIC STARTING MATERIAL WHEN PYROLYZED WITH AND WITHOUT SODIUM THIOSULFATE (NONVOLATILE = 100% - VOLATILE)

	Volatiles	
	Experimental, %	Predicted, %
Sodium gluconate	63.7 65.0	
Vanillic acid	89.4 89.4	
Sodium gluconate + $Na_2S_2O_3$	62.9	
Vanillic acid + $Na_2S_2O_3$	99.5	
Vanillic acid + sodium gluconate	83 82.3	76.9 76.9

SULFUR VOLATILIZATION

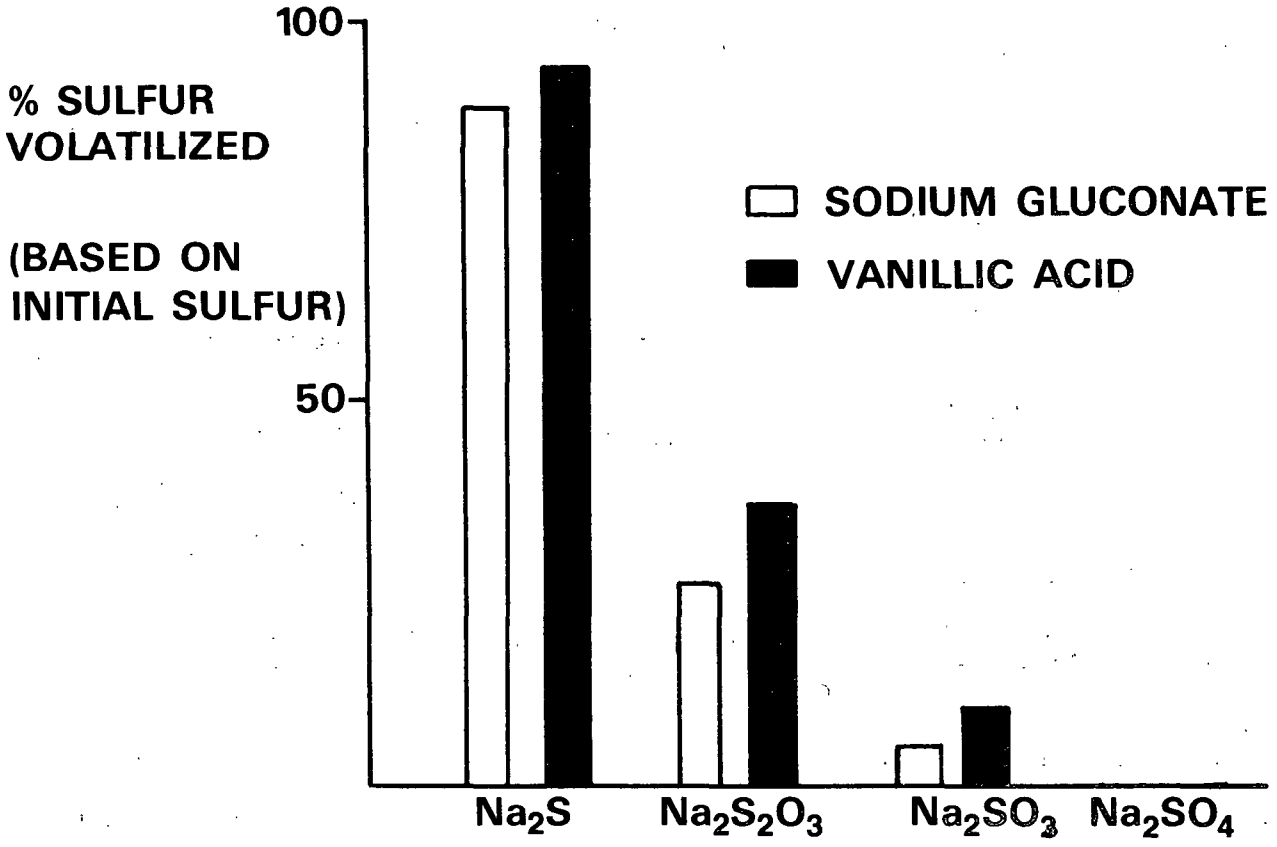
The amount of sulfur volatilized during pyrolysis was strongly dependent on the initial form of sulfur. Figure 18 compares sulfur volatilization for pyrolyses of sodium gluconate and vanillic acid with different inorganic sulfur compounds. Almost all of the sulfide sulfur and about one-third of the thiosulfate were volatilized. This figure indicates that the volatilization of sulfur was less dependent on organic material than on inorganic sulfur form. However, Fig. 18 shows that slightly more sulfur was volatilized during vanillic acid pyrolysis than during pyrolysis of sodium gluconate. In addition, a statistically significant amount of volatilized sulfur was formed from sulfite only when pyrolyzed with vanillic acid. A statistical analysis of the volatilization data is presented in Appendix III.

The sulfur volatilization results of this study show a distinct difference between the pyrolysis behaviors of sodium sulfide and sodium thiosulfate. This difference was not observed in the study performed by Douglass and Price. They observed similar proportions of sulfur volatilized as H_2S from sulfide and thiosulfate, suggesting a similar sulfur volatilization mechanism. Possible reasons for this difference in results are discussed in the following section.

SODIUM SULFIDE PYROLYSIS

Almost all (90% to 97%) of the sulfide sulfur was volatilized during pyrolysis with either sodium gluconate or vanillic acid. The results of sulfide pyrolysis runs are summarized in Table XI. The major product was H_2S. A small amount of sulfur remained in the char as sulfide and organic sulfur. These are the expected products if the dominant sulfur volatilization reaction was:

$$Na_2S(s) + H_2O(g) + CO_2(g) \rightleftharpoons Na_2CO_3(s) + H_2S(g)$$



VOLATILIZED SULFUR*

Amount of volatilized sulfur
(95% confidence intervals)**

	Na_2S	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4
Sodium gluconate	85.3-94.6	23.6-30.2	-1.8-11.3	-8.6-4.5
Vanillic acid	91.8-101.1	36.5-44.1	2.9-16.1	-13.8-(-0.6)

*The graph indicates the average sulfur volatilization; the table gives the 95% confidence intervals.
**Calculated from data in Appendix III. All values are expressed as percentages of the initial sulfur.

Figure 18. Amount of sulfur volatilized during pyrolysis with sodium gluconate or vanillic acid with an inorganic sulfur source.

TABLE XI

SULFIDE PYROLYSIS PRODUCTS
13°C/minute heating rate

Organic	Sodium Gluconate, %	Vanillic Acid, %
Volatilized[a] sulfur	85-95	95-97
Char sulfur[b] forms	Sulfide, 60	Sulfide, 75
Approximate gas[b] composition	H_2S, 100	H_2S, 96 CH_3SH, 2 $(CH_3)_2S$, 1 CS_2, 1

[a]In Tables XI, XII, XIII, and XIV, volatilized sulfur is reported as percentage of initially present sulfur.
[b]Expressed as percentage of total sulfur within that phase.

Hydrated sodium sulfide is stable to much higher temperatures than those employed in this study. The hydrates can react quickly with carbon dioxide to form sodium carbonate and hydrogen sulfide by the above reaction. The thermodynamics of this reaction (shown in Fig. 17, page 43) predict nearly complete sulfur volatilization at low temperatures.

Carbon dioxide has been shown to be a major pyrolysis product from oxygen-containing organics. If only one molecule of CO_2 is produced per molecule of vanillic acid or sodium gluconate during pyrolysis, there would be three times the stoichiometric amount of CO_2 necessary to volatilize all the sulfide. Total sulfur volatilization, however, is not thermodynamically predicted at the temperatures where pyrolysis CO_2 appears; some sulfide should remain in the char.

The experimental results are in complete agreement with what is known about the postulated reaction. This reaction was concluded to be the dominant volatilization reaction during pyrolysis of sodium sulfide with either organic compound.

The pyrolysis results of Douglass and Price, however, are not consistent with the above mechanism. They found only 37% of the sulfide volatilized as H_2S when pyrolyzed with soda lignin, whereas 60% was volatilized with glucose. These are much lower yields than are predicted from the kinetics and thermodynamics of the above reaction.

Sulfide is readily oxidized by air to thiosulfate especially if hydrated. It is possible that their sulfide had been oxidized prior to pyrolysis. Douglass and Price obtained similar sulfur volatilization results for both sulfide and thiosulfate pyrolysis. This is discussed further in the section dealing with thiosulfate pyrolysis.

SODIUM SULFATE PYROLYSIS

Sodium sulfate is generally thought to be inert under pyrolysis conditions. This study, however, indicated that sulfate was not completely inert; a small amount of sulfur was volatilized during pyrolysis (as indicated by gas analysis). The sulfur volatilized from total solid sulfur was not statistically significant.

The pyrolysis products are summarized in Table XII. Sodium sulfate was the major product. The small amount of volatilized sulfur was principally SO_2.

The observation that sulfate is not completely inert during pyrolysis is of interest. Since sulfate is not usually reduced until very high temperatures are reached, the SO_2 may be produced by direct decomposition of the sulfate. The mechanism of this reaction merits further study. However, the mechanism is of little importance to this study, since very little sulfur is volatilized during sulfate pyrolysis.

TABLE XII

SULFATE PYROLYSIS PRODUCTS
13°C/minute heating rate

Organic	Sodium Gluconate, %	Vanillic Acid, %
Volatilized sulfur	2-4	0-1
Char sulfur forms	Sulfate	Sulfate
Approximate gas composition	SO_2, 70 H_2S, 20 COS, 4 $(CH_3)_2S$, 3 CS_2, 3	SO_2, 70 CH_3SH, 20 H_2S, 10

SODIUM SULFITE PYROLYSIS

The sodium sulfite pyrolysis products are summarized in Table XIII. Sodium sulfite produced volatile sulfur only when pyrolyzed with vanillic acid, and the only form was SO_2. This result is inconsistent with the results of Douglass and Price, Table V. They observed only H_2S and found that more formed during pyrolysis of sulfite with glucose (6%) than with alkali lignin (1%).

The difference could be due to the different organics employed in the respective studies or the different heating rates and temperatures. The experiments of Douglass and Price (52) employed a higher heating rate and temperature than those in this study. These more severe conditions would be expected to increase sulfur volatilization. This study, however, found almost 10% of the initial sulfite volatilized with vanillic acid, whereas none was volatilized with sodium gluconate. These results lead one to conclude that the results are due to the different organics employed for pyrolysis, and not the pyrolysis conditions.

TABLE XIII

SULFITE PYROLYSIS PRODUCTS
13°C/minute heating rate

Organic	Sodium Gluconate	Vanillic Acid, %
Volatilized sulfur		10
Char sulfur forms	Sulfite	Sulfite
Approximate gas composition	--	SO_2, 100

One difference between the two organics used in this study is that one is a free acid and the other is a sodium salt. Acids are known to strip SO_2 from sulfite solutions. Vanillic acid and sodium sulfite moistened with distilled water and heated were found to emit SO_2. Under pyrolysis conditions vanillic acid may react directly with sulfite to strip off SO_2, forming sodium vanillate. Water liberated during pyrolysis may aid this reaction.

SODIUM THIOSULFATE PYROLYSIS

The most complex and interesting reactions occur during the pyrolysis of mixtures containing $Na_2S_2O_3$. This is apparent from the large variety of pyrolysis products shown in Table XIV.

Pyrolysis of thiosulfate with sodium gluconate or vanillic acid led to substantially different pyrolysis gases. Hydrogen sulfide was the principal sulfur gas produced during sodium gluconate pyrolysis. The principal sulfur gas produced during pyrolysis of thiosulfate with vanillic acid was SO_2; the rest of the gas was a mixture of organic reduced sulfur compounds.

TABLE XIV

THIOSULFATE PYROLYSIS PRODUCTS
13°C/minute heating rate

Organic	Sodium Gluconate, %	Vanillic Acid, %
Volatilized sulfur	20-35	30-45
Char sulfur forms	Sulfide, 60	Sulfide, 45
	Polysulfur, 17	Polysulfur, 45
	Unextractable sulfur, 20	Unextractable sulfur, 5
	Sulfate, 3	Sulfate, 5
Approximate gas composition	H_2S, 90	SO_2, 50
	SO_2, 10	H_2S, 17
		CH_3SH, 13
		$(CH_3)_2S$, 9
		CS_2, 9

The thiosulfate reactions are best understood in terms of a simple reaction model. The model includes two low-temperature reactions and a higher temperature thermal decomposition reaction. The low-temperature reactions consist of a thiosulfate acidic decomposition to sulfur dioxide and elemental sulfur and a thiosulfate reduction to sulfide and elemental sulfur. The elemental sulfur can react with the organic pyrolysis products or directly with the organic substrate itself to produce volatile and nonvolatile organic reduced sulfur compounds. Some elemental sulfur formed by these reactions remains in the residue as polysulfur.

The reaction model of thiosulfate is summarized below; only the routes of sulfur and thiosulfate are shown:

$$Na_2S_2O_3 \xrightarrow{1} SO_2 + S^o \qquad \text{low temperature}$$

$$\xrightarrow{2} Na_2S + S^o \qquad \text{low temperature}$$

$$\xrightarrow{3} \frac{3}{4} Na_2SO_4 + \frac{1}{4} Na_2S_5 \qquad \text{high temperature}$$

$$So \xrightarrow{4} \text{organic reduced sulfur compounds}$$

The acidic decomposition of thiosulfate to sulfur dioxide and elemental sulfur [Reaction (1)] usually takes place in aqueous solution. It had to be determined whether or not this reaction was possible under the pyrolysis conditions employed in this study. This postulated decomposition to sulfur dioxide and elemental sulfur intermediates was explored by pyrolyzing mixtures of an organic with sulfur forms similar to the postulated intermediates and observing the gaseous pyrolysis products. A pyrolysis gas composition similar to the thiosulfate pyrolysis gas compositions would indicate that thiosulfate did decompose to SO_2 and S^o during pyrolysis. The compounds used as intermediates were sodium sulfite and elemental sulfur. The pyrolyses were carried out as before, with equal amounts of sulfur in each form.

The results of these pyrolyses of the mixtures are shown in Table XV. The vanillic acid pyrolysis reported in the table appeared to agree with the results of vanillic acid and thiosulfate, reported in Table XIV. The principal sulfur gas product was SO_2, with the remainder of the gas consisting of a mixture of reduced sulfur compounds. The sodium gluconate mixture pyrolysis results did not agree as well with the earlier thiosulfate results, although SO_2 was produced. The overall results do indicate that the decomposition of thiosulfate to sulfur dioxide and elemental sulfur was possible during pyrolysis.

Reaction (1), based on an acidic decomposition usually associated with aqueous solution, would be expected to occur early in the pyrolysis when the first organic pyrolysis products, an aqueous distillate and organic acids, appear. An example of the reaction might be:

$$CO_2 + Na_2S_2O_3 \longrightarrow Na_2CO_3 + SO_2 + S^o$$

TABLE XV

RESULTS OF MIXTURES CONTAINING SODIUM SULFITE AND ELEMENTAL SULFUR
23°C/minute = heating rate

Organic	Sodium Gluconate, %	Vanillic Acid, %
% Sulfur volatilized	45	55
Approximate gas composition	H_2S, 82 SO_2, 12 CH_3SH, 5 COS, 1 No sulfide in char	SO_2, 34 H_2S, 27 CH_3SH, 19 $(CH_3)_2S + CS_2$, 18 COS, 1 Sulfide in char

Such a reaction sequence would indicate that SO_2 should be the first observed volatile sulfur form. The time sequences of thiosulfate pyrolysis sulfur-gas products are tabulated in Appendix IV. These results do indicate that the SO_2 started to appear early during the pyrolysis, usually preceding the appearance of the reduced sulfur gases. This was especially apparent during the vanillic acid pyrolyses, where the acidic decomposition was the predominant sulfur volatilization reaction.

The next higher temperature, organic pyrolysis products include the noncondensible combustible volatiles such as H_2 and CO. These compounds are capable of reducing the thiosulfate to sulfide and elemental sulfur, Reaction (2). An example of this reaction is:

$$Na_2S_2O_3 + 3CO \rightleftharpoons Na_2S + S^o + 3CO_2$$

$$\Delta H = -25.1 \text{ kcal/mole}$$

$$\Delta G = -28.0 \text{ kcal/mole}$$

This reduction occurs during the latter stage of organic pyrolysis. The sulfide formed by this reaction would not be volatilized to as great an extent as observed

during sulfide pyrolysis. Most of the water and carbon dioxide necessary for hydrogen sulfide stripping would have already been released. Most of the sulfide would, therefore, remain in the char, accounting for the large amount of sulfide experimentally observed in the thiosulfate pyrolysis chars.

The relative importance of Reactions (1) and (2) depends on the pyrolysis behavior of the organic component. Thermogravimetric analysis of the organic starting materials used in this study indicated that in the presence of thiosulfate, vanillic acid decomposed between 140°C and 230°C; sodium gluconate decomposed between 200°C and 280°C. Since vanillic acid decomposed at lower temperatures than sodium gluconate, the lower temperature decomposition of thiosulfate by Reaction (1) would be expected to be more important during vanillic acid pyrolysis than during sodium gluconate pyrolysis. Therefore, more SO_2 would be expected during vanillic acid pyrolysis than during sodium gluconate pyrolysis. This was experimentally observed.

The elemental sulfur formed during Reactions (1) and (2) can react with the organic substrate or pyrolysis products as an oxidant [Reaction (4)], producing volatile and nonvolatile organic reduced sulfur compounds and sulfide. The remaining elemental sulfur will be retained as polysulfur.

Any thiosulfate remaining in the char after the organic material finished reacting would thermally decompose to sulfate and polysulfide by Reaction (3).

The reaction model that has been developed can be used to calculate the amounts of sulfide, polysulfur, total residual sulfur, and the amount of reduced sulfur gas from the amounts of sulfate in the solid residue and the amount of sulfur dioxide in the pyrolysis gas. By making the following assumptions, the model was used to interpret the experimental thiosulfate pyrolysis data.

1) All sulfate originates from the thiosulfate thermal decomposition reaction, Reaction (3).

2) All the sulfur dioxide is produced by Reaction (1).

3) One-half of the elemental sulfur is volatilized; the other half remains in the solid phase as organic sulfur, polysulfur, or sulfide. Since nothing is known about these reactions and what determines the split between volatile and nonvolatile organic sulfur, this assumption gives equal probability to both.

The model calculations are compared with the experimental results in Table XVI.

The numbers shown in Table XVI are computed as follows: the data from Pyrolysis 39 are used as an example. The sulfate, assumed to originate entirely from Reaction (3), is used to calculate the amounts of sulfide and polysulfur also formed by this reaction. For example, the char from Pyrolysis 39 contained 4.8% of the initial sulfur as sulfate. The stoichiometry of Reaction (3) indicates that 37.5% of the thermally decomposed thiosulfate sulfur is sulfate, 12.5% is sulfide, and 50% is polysulfur. On the basis of the amount of sulfate produced, 4.8%, the amount of sulfide produced by this reaction equalled 1.6% of the initially present sulfur, whereas 6.4% of the initially present sulfur appeared as polysulfur.

All SO_2 is assumed to originate from Reaction (1). For Pyrolysis 39, 3.1% of the initial sulfur was found as SO_2. The stoichiometry of Reaction (1) indicates that 3.1% of the initial sulfur also appeared as elemental sulfur.

The remaining thiosulfate was reduced to sulfide and elemental sulfur. This corresponds to 81% of the initial sulfur reduced to Na_2S and S^o by

$$100\% - 4.8\%(SO_4^{-2}) - 1.6\%(S^{-2}) - 6.4\%(S_x) - 3.1\%(SO_2) - 3.1\%(S^o) = 81\%$$

Reaction (2) for Pyrolysis 39. This is distributed equally between Na_2S and S^o by the reaction stoichiometry, 40.5% S^{-2} and 40.5% S^o.

TABLE XVI

COMPARISON OF EXPERIMENTAL THIOSULFATE PYROLYSIS RESULTS WITH POSTULATED MODEL. EXPERIMENTAL VALUES ARE IN PARENTHESES. ALL NUMBERS ARE PERCENTAGES OF INITIAL SULFUR

Pyrolysis	Theoretical Yields From Reaction (3)			Theoretical Yields From Reaction (1)		Theoretical Yields based on Reaction (2)		Total $S^=$	Total Solid Sulfur	Reduced Sulfur Gases	Sulfur Balance Closure, %
	$SO_4^=$	$S^=$	S_x	SO_2	S^o	$S^=$	S^o				
39	(4.8)	1.6	6.4 (13)	(3.1)	3.1	40.5	40.5	42.1 (42)	75.1 (69.1)	21.8 (9.0)	(82)
52	(4.6)	1.5	6.1 (11)	(3.6)	3.6	40.3	40.3	41.8 (40)	74.5 (71.7)	22.0 (20.0)	(96)
54	(4.7)	1.6	6.3 (13)	(1.9)	1.9	41.8	41.8	43.4 (38)	76.3 (68.7)	21.9 (14.0)	(85)
40	(14.9)	5.0	19.9 (23)	(1.4)	1.4	28.7	28.7	33.7 (35)	83.6 (80.5)	15.0 (5.0)	(87)
44	(15.2)	5.1	20.3 (18)	(2.2)	2.2	27.7	27.7	32.6 (37)	83.0 (79.9)	14.9 (8.0)	(90)
45	(24.6)	8.2	32.8 (16)	(8.6)	8.6	8.6	8.6	16.8 (29)	82.8 (78.2)	8.6 (9.0)	(96)
47	(4.4)	1.5	5.9 (9)	(13.2)	13.2	30.9	30.9	32.4 (32)	63.9 (66.6)	22.1 (22)	(102)
80 & 50	(2.1)	0.7	2.8 (35)	(27.3)	27.3	20.2	20.2	20.9 (32)	49.6 (57.6)	23.8 (15.0)	(107)

The total amount of sulfide sulfur is the sum of that produced by Reactions (2) and (3). This equals 42.1% for Pyrolysis 39. The total solid sulfur is

$$1.6\% + 40.5\% = 42.1\%$$

equal to the sum of the sulfate, sulfide, polysulfur, and one-half the elemental sulfur (assumed). This equals 75.1% of the initial sulfur remaining in the char for Pyrolysis 39:

$$4.8\% + 42.1\% + 6.4\% + \frac{1}{2}(40.5\% + 3.1\%) = 75.1\%$$

The other half of the elemental sulfur, $\frac{1}{2}(40.5\% + 3.1\%) = 21.8\%$ for Pyrolysis 39, produced reduced sulfur gases.

The numbers shown in parentheses in Table XVI are the experimental data. They are presented so that a comparison can be made between the calculated and experimentally obtained values for the amounts of sulfide, polysulfur, and total sulfur in the solid char and the amount of reduced sulfur gases.

The model's predictions are closest to the experimental results for the sulfide sulfur and the total solid residue sulfur. The calculated polysulfide sulfur quantities are generally lower than those observed experimentally. The formation of polysulfur from elemental sulfur has not been numerically considered in the model and may account for some of the differences. The amounts of reduced sulfur gases are in fair agreement with the model, approaching closest when the sulfur balance closes well. Overall, the experimental results are well represented by the simple model.

The thiosulfate results of Douglass and Price are consistent with this model, although they only analyzed for the formation of H_2S. The model indicates that during thiosulfate pyrolysis any H_2S formed must have been produced from elemental sulfur. Douglass and Price pyrolyzed elemental sulfur with soda lignin and obtained

a 75% yield of sulfur as H_2S. Assuming all of their thiosulfate decomposed by either Reaction (1) or (2) of the model, one-half of the thiosulfate would have become elemental sulfur, of which 75% was expected to produce H_2S. The model predicts:

$$(2 \text{ millimoles } S_2O_3^{=}) \times \left[\frac{0.75 \text{ mole } H_2S^{*}}{\text{mole } S^{o}}\right] \times \left[\frac{0.5 \text{ mole } S^{o}{}^{**}}{\text{mole } S_2O_3}\right] = 0.75 \text{ millimole } H_2S$$

Douglass and Price observed 0.786 millimole and 0.736 millimole of H_2S produced during the pyrolysis of thiosulfate with soda lignin.

Their sulfide results are most readily interpreted by assuming that their sulfide had been oxidized to thiosulfate prior to pyrolysis. Then the model predicts:

$$(2 \text{ millimoles } S^{=}) \times \left[\frac{0.5 \text{ mole } S_2O_3^{=}{}^{***}}{\text{mole } S^{=}}\right] \times \left[\frac{0.5 \text{ mole } S^{o}{}^{**}}{\text{mole } S_2O_3^{=}}\right] \times \left[\frac{0.75 \text{ mole } H_2S^{*}}{\text{mole } S^{o}}\right] =$$

$$0.375 \text{ millimole } H_2S$$

They observed 0.370 millimole of H_2S produced.

The Douglass and Price results for the pyrolysis of elemental sulfur with glucose are not readily interpreted. This study indicated that the initial presence of elemental sulfur during the pyrolysis of sodium gluconate influenced its pyrolysis. Similar events may have taken place during the pyrolysis of glucose and elemental sulfur. The reactions of elemental sulfur are not well understood.

If the described model is taken to be representative of thiosulfate pyrolysis behavior, then the low-temperature reactions - Reactions (1) and (2) - are competing for thiosulfate during the decomposition of the organic. These two competing reactions

*75% of the elemental sulfur produced H_2S. This was observed by Douglass and Price.

**Reaction (1) or (2) of the model indicates that each mole of thiosulfate produces 0.5 mole of elemental sulfur.

***From the stoichiometry of the oxidation reaction: $2\ Na_2S + 2\ O_2 \rightarrow Na_2S_2O_3 + Na_2O$.

are expected to have different kinetics. Different heating rates would therefore affect the two reactions differently. A heating rate effect was clearly seen in the pyrolysis of thiosulfate with sodium gluconate.

At the 13°C/minute temperature rise, the pyrolysis of sodium thiosulfate with sodium gluconate produced hydrogen sulfide as the principal volatile sulfur form. At the 23°C/minute temperature rise, sulfur dioxide became the dominant sulfur gas. This is shown in Fig. 19. During vanillic acid pyrolysis, SO_2 production again increased with heating rate but not to the same extent as with sodium gluconate; SO_2 production was the dominant reaction during vanillic acid pyrolysis.

The results indicate that there are competing reactions and that at a higher heating rate there is a shift in reaction kinetics away from the reduction of thiosulfate to the postulated decomposition of thiosulfate to SO_2 and S^o. This shift does not occur during vanillic acid pyrolysis, since the acidic decomposition already dominates at the lower heating rate.

EFFECT OF HEATING RATE

The most important heating rate effect was the observed change in product gas composition during sulfur volatilization. This was described in the previous section.

The effect of heating rate on sulfur volatilization itself is shown in Table XVII. Heating rate had a generally negligible effect on the amount of volatilized sulfur.

Swelling was observed during all pyrolyses of sodium gluconate. Vanillic acid pyrolysis was not generally characterized by swelling except when pyrolyzed with sulfide. The extent of swelling was inversely proportional to the heating rate. The chars produced at the higher heating rate were denser than those produced at the low heating rate.

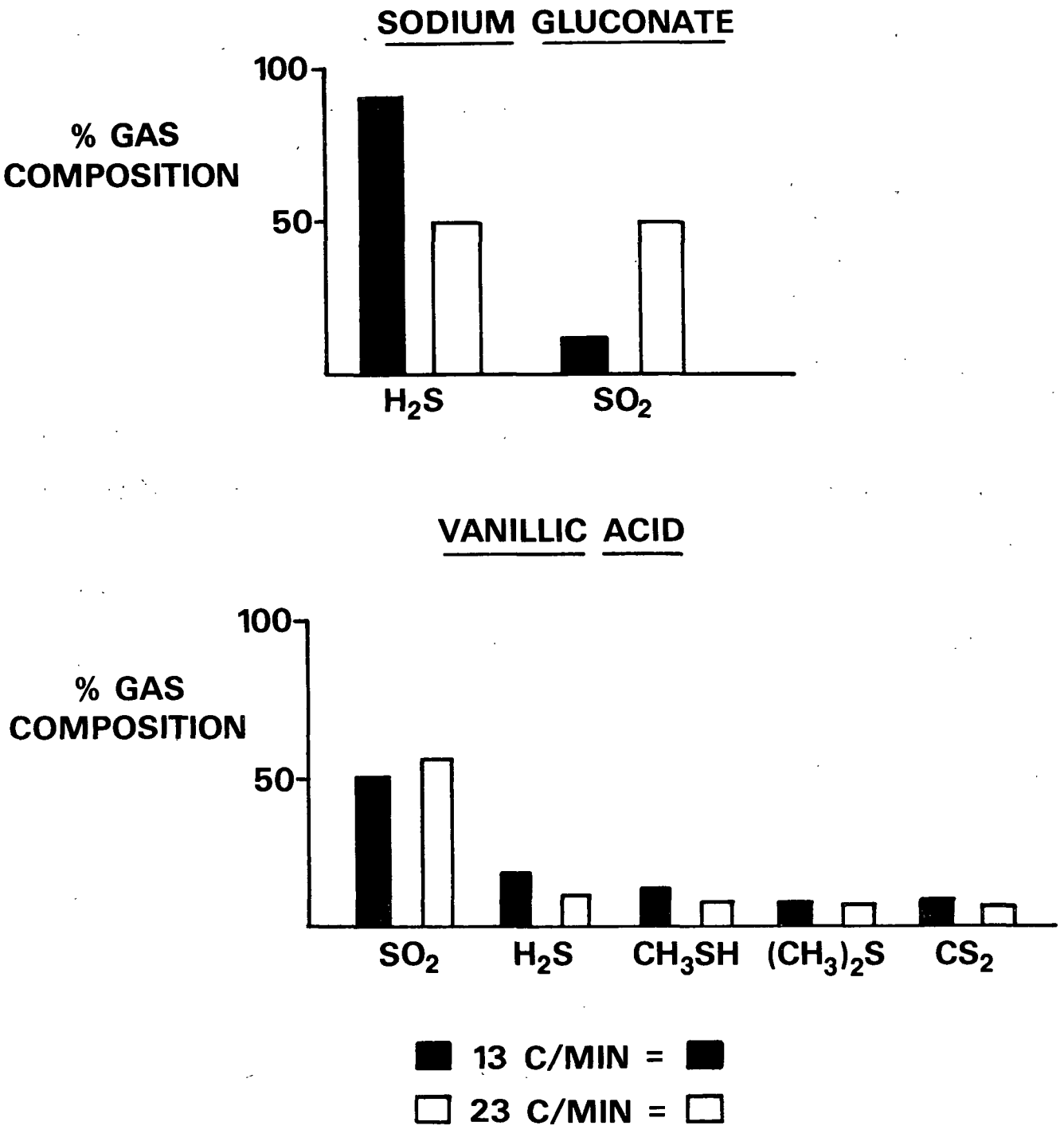


Figure 19. Effect of heating rate on gas composition from thiosulfate pyrolysis.

TABLE XVII

SULFUR VOLATILIZATION AS FUNCTION OF HEATING RATE

	% Sulfur Volatilized			
Sodium Gluconate, °C/minute	Na_2S, %	$Na_2S_2O_3$, %	Na_2SO_3, %	Na_2SO_4, %
13	89	22-35	0.0	~2
23	91	20-30	0.0	~4
Vanillic Acid, °C/minute				
13	96.5-97.5	35-45	7.5	~1
23	95.5-96.5	35-45	10	~0.5

EFFECT OF PARTICLE SIZE

The effect of particle size on sulfur volatilization is given in Table XVIII for sodium sulfide and sodium thiosulfate. Particle size has a negligible effect on the volatilization of sulfur during sodium sulfide pyrolysis. The only significant effect of particle size was found during sodium thiosulfate pyrolysis; more sulfur is volatilized from the smaller 45-100 mesh particles.

TABLE XVIII

SULFUR VOLATILIZATION AS FUNCTION OF PARTICLE SIZE

Sodium Gluconate, mesh	% Sulfur Volatilized	
	Na_2S	$Na_2S_2O_3$
28-45	89-92	20-25
45-100	89-91	30-35
Vanillic acid, mesh		
28-45	96-98	30-35
45-100	95-96	45

EFFECT OF PURGE RATE

The nitrogen purge gas served two functions: (1) removal of pyrolysis gas from the hot reactor and (2) dilution of it. Both functions served to minimize secondary

reactions among the product gases. It was expected that the purge rate would affect the sulfur gas product distribution. The effects of purge gas flow rate on the sulfur gas product distribution as observed experimentally are shown in Table XIX. The purge rate had no effect on the pyrolysis of sodium gluconate with thiosulfate. There did appear to be a small effect for the vanillic acid pyrolysis. Purge rate effects were minimized by maintaining the purge gas flow rate constant for all other pyrolyses.

TABLE XIX

EFFECT OF PURGE RATE ON GASEOUS SULFUR PRODUCT DISTRIBUTION

Purge Rate, cm^3/sec	12.0	16.3	29.8
Sodium Gluconate + Sodium Thiosulfate			
H_2S	75.4	79.5	73.7
COS	3.7	3.3	2.7
SO_2	11.9	11.6	15.2
CH_3SH	5.4	2.0	4.5
Other	3.6	3.6	3.9
	100.0	100.0	100.0
Vanillic Acid + Sodium Thiosulfate			
H_2S	9.8	14.0	17.7
COS	1.0	0.2	0.7
SO_2	60.0	65.2	50.2
CH_3SH	9.7	6.9	12.8
Other	19.2	13.3	18.6
	100.0	100.0	100.0

SUMMARY AND CONCLUSIONS

The formation of volatile sulfur compounds from sodium sulfide, sodium thiosulfate, sodium sulfite, and sodium sulfate was studied during pyrolysis with sodium gluconate and vanillic acid. The amounts and forms of the volatilized sulfur were found to be primarily dependent on the inorganic sulfur compound, the organic material, and the inorganic particle size. Heating rate and nitrogen purge rate appeared to have a minor effect on the amount of volatile sulfur compounds formed. Heating rate did, however, affect the gaseous sulfur product distribution.

The largest amounts of volatile sulfur were produced during pyrolysis of sodium sulfide or sodium thiosulfate with either organic material. Sodium sulfite produced volatile sulfur, principally SO_2, only when pyrolyzed with vanillic acid. The reaction mechanism was postulated to be a direct reaction of the sulfite with the vanillic acid to strip away SO_2. Sodium sulfate produced a small amount of volatile sulfur, as indicated by gas chromatography. However, this small amount was statistically insignificant when based on the solid sulfur analyses.

The Na_2S pyrolysis results were explained by the stripping away of hydrogen sulfide by the action of H_2O and CO_2 resulting from the pyrolytic degradation of the organic. The reaction was represented:

$$Na_2S(s) + H_2O(g) + CO_2(g) \rightleftharpoons Na_2CO_3(s) + H_2S(g)$$

The thermodynamics of the above reaction was shown to favor total volatilization of the sulfur at temperatures below 300°C. Since total volatilization was not observed, it was concluded that the pyrolytic decomposition of the organic was the rate-limiting step.

Sodium thiosulfate pyrolysis behavior was determined to be best represented by a three-reaction model. The first two reactions consist of a low-temperature acidic

decomposition of the thiosulfate to SO_2 and elemental sulfur, and a reduction of the thiosulfate to Na_2S and elemental sulfur. The pyrolysis behavior of the organic compound affects only the relative rates of each reaction. Any thiosulfate which remained after the organic was totally decomposed underwent thermal decomposition to sulfate and polysulfide above 400°C. This behavior of thiosulfate sulfur is summarized below:

$$Na_2S_2O_3 \xrightarrow{1} SO_2 + S^o$$
$$\xrightarrow{2} Na_2S + S^o$$
$$\xrightarrow{3} \frac{3}{4} Na_2SO_4 + \frac{1}{4} Na_2S_5$$

The applications of the reaction mechanisms described for thiosulfate and sulfide are not necessarily limited to the systems employed in the present study. For example, because of the highly alkaline nature of kraft black liquors, the acidic decomposition of thiosulfate would not be expected to be an important reaction. Instead, the two most probable reactions of thiosulfate during black liquor pyrolysis would be reduction to Na_2S and elemental sulfur, or thermal decomposition to Na_2SO_4 and Na_2S_5. Although such extrapolation was not an objective of this thesis study, it can be concluded that this study has provided a firm foundation for future black liquor pyrolysis studies.

The results of this study indicate that Feuerstein's assumption was in error. Feuerstein assumed that the initial form of sulfur had no influence on the final pyrolysis sulfur distribution. This study shows that not only does the initial sulfur form control the amount of sulfur volatilized, but it also determines what compounds would be principally formed.

The results of this study also indicate the existence of problems in the data of Douglass and Price. Their results suggested that sodium sulfide and sodium

thiosulfate had similar pyrolysis behaviors. The present study clearly indicates that sodium sulfide and sodium thiosulfate display very different pyrolysis behaviors. There are several possible reasons why the results of Douglass and Price could be in error. Interpretation of their results in light of the thiosulfate pyrolysis model developed in this study suggests that their sulfide may have been oxidized to thiosulfate prior to pyrolysis.

ACKNOWLEDGMENTS

My sincere thanks are extended to my thesis advisory committee - Dr. Thomas M. Grace (chairman), Dr. Dwight B. Easty, and Dr. Wm. James Frederick - for their guidance, criticism, and patience. Their help made this thesis work a true learning experience. I am especially grateful to Dr. Grace, whose many ideas and insights allowed this thesis to take shape.

Many others also contributed to the completion of this thesis. I am indebted to David Kielpikowski for much advice and help with analytical procedures. Bruce Andrews is thanked for his suggestions and ideas. I am grateful to Paul F. Van Rossum and Marvin C. Filz, Jr., for construction of my equipment.

Many others not directly involved with the thesis nevertheless contributed to its successful completion. Dr. Gary Baum and his wife, Paula, are thanked for their friendship and encouragement. Special thanks go to my wife, Irene, for her love and moral support. Finally, to my parents, whose support, encouragement, and love throughout the years have made my study possible, thank you.

The Institute of Paper Chemistry and its member companies are thanked for the financial assistance that made this work possible.

LITERATURE CITED

1. Lin, K. H., Annual Review of Industrial and Engineering Chemistry 2:296-344 (1974).

2. Gutsch, D. C., and Pasto, D. G., Fundamentals of Organic Chemistry. Prentice Hall, New York, 1975.

3. Recovery of Pulping Chemicals A-207 course notes, The Institute of Paper Chemistry, Appleton, WI.

4. Passinen, K. Chemical Composition of Spent Liquors. Proc. IUPAC EUCEPA Symp., Recovery of Pulping Chemicals, Helsinki, 1968.

5. Sjostrom, E., Tappi 60(9):151-4(1977).

6. Pearl, I. A., The Chemistry of Lignin. Marcel Dekker, Inc., New York, 1967.

7. Brauns and Brauns, The Chemistry of Lignin-supp., Academic Press, New York, 1960.

8. Rydholm, S. A., Pulping Processes. John Wiley and Sons, New York, 1965.

9. Enkvist, T., Paperi Puu 43(11):657-62(1961).

10. Enkvist, T., Ashorn, T., Hastbacka, K., Paperi Puu 44(8):395-404(1962).

11. Blackwell, B. R., et al. Tappi 62(10):33-7(1979).

12. Douglass, I. B., Price, L., Tappi 49(8):335-42(1966).

13. McKean, W. T., Jr., et al. Tappi 50(8):400-5(1967).

14. Sarkanen, K. V., et al. Tappi 53(5):766-83(1970).

15. Hagglund, E. Chemistry of Wood. Academic Press, Inc., New York, 1951.

16. Browne, F. L. Theories of the combustion of wood and its control. USDA FPL No. 2136, Forest Prod. Lab., Madison, WI, 1963.

17. Shafizadeh, F. Pyrolysis and combustion of cellulosic materials. Adv. Carbohyd. Chem. 23:419(1968).

18. Molton, P. M., and Demmitt, T. F. Reaction mechanisms in cellulose pyrolysis - a literature review. Battelle, Pacific Northwest Lab., Richland, WA, 1978.

19. Ohnishi, A., Kato, K., and Takagi, E. Curie-point pyrolysis of cellulose. Polymer J. 7(4):431-7(1975).

20. Beall, F. C., and Eickner, H. W. Thermal degradation of wood components. USDA FPL No. 130, Forest Prod. Lab., Madison, WI, 1970.

21. Garniner, D., J. Chem. Soc. (C):1473-6(1966).

22. U.S. Forest Service Research Paper, FPL No. 71, Forest Prod. Lab., Madison, WI, 1967.

23. Chemical and Engineering News, March 3, 1980.

24. Hurd, I. E. The pyrolysis of carbon compounds. Chemical Catalog Company, New York, 1929.

25. Wise, L. E., and Jahn, F. L., Wood Chemistry, 2nd ed. Vol. I, II Reinhold Publishing Co., New York, 1952.

26. Heuser, F. The Chemistry of Cellulose. John Wiley and Sons, Inc., London, 1944.

27. Shimzu, K., Bull. Govt. Forest Expt. Sta., Tokyo (272):1-78(1975).

28. Morrison, R. T., and Boyd, R. N., Organic Chemistry, 2nd ed., Allyn and Bacon, Inc., Boston, 1972.

29. Allen, G. G., and Mattile, T., In Sarkanen, K. V., Ludwig, C. H., eds. Lignin, Chapter 14, Wiley-Interscience, 1971.

30. Domburg, G. E., Izv. Akad. Nauk. Latv. SSR, Ser. Khim. (6):734-7(1974).

31. Cladkova, N. Y., et al., Khim. Ispol'z Lignina 1974:434-40.

32. Kislitsyn, A. N., et al., Khim. Ispol'z Lignina 1974:381-9.

33. Wood Technology: Chemical Aspects, Goldstein, I. S., ed., ACS Symp. Series No. 43, Washington, DC, 1977.

34. Thermal Uses and Properties of Carbohydrates and Lignins, Shafizadeh, F., Sarkanen, K. V., Tillman, D. A., eds. Academic Press, New York, 1976.

35. Attar, A., Fuel 57(4):201-12(1978).

36. Chemistry of Coal Utilization, Vol. I and II, prepared by the committee on utilization of coal, Lowry, H. H., chairman, John Wiley and Sons, New York, 1945.

37. Attar, A., Corcoran, W. H., Ind. Eng. Chem., Prod. Res. Dev. 16(2):168-70 (1977).

38. Energy Technology Handbook, Considine, D. M., ed., McGraw-Hill, Inc., 1977.

39. Perry, R. H., and Chilton, C. H., Chemical Engineer's Handbook, 5th ed., McGraw-Hill Co., New York, 1973.

40. Corey, R. C. Elements of Coal Science and Utilization Technology, and Energy Facts and Figures, U.S. Department of Energy, Washington DC, 1978.

41. Van Krevelen, D. W. Coal. Elsevier Publ. Co., New York, 1961.

42. Francis, W., Coal. Edward Arnold Publishers, Ltd. London, 1961.

43. Mukherjee, S. N., FRI News 27(1):19-22(1977).

44. Stinnett, S. J., Harrison, D. P., Pike, R. W., Environ. Sci. Technol. 8(5):441-4(1974).

45. Yergey, A. L., et al., Ind. Eng. Chem., Process Devt. 13(3):233-40(1974).

46. Bjorkman, Pyrolysis of Spent Liquors, Helsinki Symposium on Recovery of Pulping Chemicals, 1967.

47. Monaghan, M. T., Siddall, R. G., Tappi 46(2):89-91(1963).

48. Feuerstein, D. L., Ph.D. Thesis, University of California, Berkeley, 1966.

49. Feuerstein, D. L., Thomas, J. F., Brink, D. L., Tappi 50(6):258-62(1967).

50. Brink, D. L., Thomas, J. F., Jones, K. H., Tappi 53(5):837-43(1970).

51. Baklien, A., Appita 14(1):5-17(1960).

52. Douglass, I. G., Price, L., Tappi 51(10):465-7(1968).

53. Prahacs, S., et al., I & EC Process Design and Devt. 6(2):180-6(1967).

54. Barclay, H. G., Prahacs, S., Pulp Paper Mag. Can. 72(2):51-64(1971).

55. Rosen, E., Svensk Kemish Tidskrift 76(4):195-209(1964).

56. Bauer, T. W., Dorland, R. M., Can. J. Tech. Vol. 32, p. 91-101.

57. Stull, D. R. and Prophet, H., JANAF Thermochemical Tables, 2nd ed., U.S. Department of Commerce, 1971.

58. Magnusson, H. and Warnquist, B., Chem. Eng. Progr. 76(2):54-6(1980).

59. Kerby, R. C., Hughson, M. R., Research Report R262, Extraction Metallurgy Division, Department of Energy, Mines and Resources, Ottawa, Canada, April 1973.

60. Sneed, M. C. and Maynard, J. L., General Inorganic Chemistry, D. Van Nostrand Co., New York, 1948.

61. Pryor, W. A. Mechanisms of Sulfur Reactions. McGraw-Hill Book Co., New York, 1962.

62. Nickin, T., Farrington, F., and Odgen D. Brit. pat. 1,459,753.

63. J. Inorg. Nucl. Chem. 1979, Vol. 38, p. 537-40 Pergamon Press, G. B.

64. Sidgwich, N. V. The Chemical Elements and their Compounds, Vol. II, University Press, Oxford, 1951.

65. Wostradowski, R. A., et al., Transactions of the Technical Section 2(2):51-7 (1976).

66. Kharasch, N., ed., Organic Sulfur Compounds, Vol. I, Pergamon Press, New York, 1961.

67. TAPPI Standard T 624 os-68.

68. TAPPI Standard T 625 ts-64.

69. Noel, D. L., Tappi 61(5):73-6(1978).

70. Souza, T. L. C., Lane, D. C., and Bhatia, S. P., Anal. Chem. 47(3):543-5(1975).

APPENDIX I

ANALYTICAL METHODS

The objective of the analytical methods described here was to account for all the initially present sulfur among the final reaction products. The materials to be analyzed for the sulfur forms present were the gases produced during the pyrolysis and the solids remaining at the end of the pyrolysis. Any liquid produced during pyrolysis was analyzed only for total sulfur. The analyses were based on TAPPI Standards T 624 os-68, T 625 ts-64 (67-68).

SOLIDS ANALYSIS

The crucible containing the pyrolysis solids was weighed to the nearest 0.1 mg. Under nitrogen, the solids were finely ground with mortar and pestle and transferred to five small covered weighing bottles. The thiosulfate, sulfite, and polysulfide analyses were carried out immediately. The solids for total sulfur analysis were stored in 5 mL of 30% H_2O_2 solution. The solids for sulfide analysis were stored in a sulfide antioxidant buffer (SAOB II) solution (69). The solids for sulfate analysis were added to concentrated HCl and evaporated to dryness for storage.

The sulfide antioxidant buffer was prepared by dissolving 67 grams disodium EDTA and 37 grams ascorbic acid in 200 mL of 10N NaOH, followed by dilution to one liter with distilled water. This solution was kept tightly stoppered and was used until it turned dark brown.

TOTAL SULFUR

An accurately weighed portion, 0.3-0.5 g, of the pyrolysis solids was transferred to a 123-mL heavy glass Erlenmeyer flask using a minimum of distilled water. Five milliliters of 30% H_2O_2 solution was added to the sample, which could now be stored.

For analysis, 40 mL of concentrated HNO_3 and a boiling chip were added. The solution was brought to boiling and allowed to boil with occasional additions of acid to maintain the volume until the solution color began to lighten. The solutions were allowed to cool to room temperature before the next step.

Forty milliliters of concentrated HNO_3 was added to the solution followed by 5 mL of 70% $HClO_4$. The Erlenmeyer flasks were placed on hot plates in a perchloric acid hood for digestion. Several additions of concentrated HNO_3 were made over the course of the digestion, since the pyrolysis solids digested slowly.

When the solution was orange or lighter colored, the HNO_3 was allowed to boil off so that the digestion with perchloric acid would take place. The oxidation was complete when the solution was colorless and dense white perchloric acid fumes were formed. After digestion the solution was allowed to cool. Five milliliters of concentrated HCl was added and the solution was reheated until the perchloric acid fumes reappeared. The solution was cooled to room temperature and 50 mL distilled water was added.

The solution was transferred to a 250-mL beaker. The volume was adjusted to 175 mL with distilled water, and a drop of methyl orange indicator was added. Concentrated NH_4OH was added dropwise until the color changed from red to yellow. Five milliliters of concentrated HCl was added and then the solution was heated to near boiling. At this point 30 mL of boiling 10% $BaCl_2$ solution were added with stirring.

The precipitate was allowed to settle for one hour, after which the solution was filtered through ashless filter paper. The precipitate was washed with at least 150 mL of warm distilled water. The filter paper and precipitate were transferred to a tared crucible, which was then placed in a 800°C muffle furnace for ignition. After two hours the crucible was cooled and weighed. The weight of sulfur in the

$BaSO_4$ was calculated. Total sulfur in the pyrolysis solids was calculated by dividing the weight of sulfur found above by the fraction of pyrolysis solids used for this analysis.

SULFATE ANALYSIS

The solids for sulfate analysis were accurately weighed and placed in a 250-mL beaker with 50 mL distilled water. Twenty milliliters of concentrated HCl was added, the beaker was covered with a watch glass and then placed on a hot plate to boil gently until the solution evaporated to near dryness.

Upon cooling, the solids were dissolved in 50 mL of distilled water. The solution was then suction filtered; any solids were discarded. The volume of filtrate was adjusted to 175 mL, and a drop of methyl orange indicator was added. Concentrated NH_4OH was added dropwise until the indicator color changed from red to yellow. Five milliliters of concentrated HCl was added, and the solution was heated to near boiling. At this point, 30 mL of boiling 10% $BaCl_2$ solution were added with stirring. The stirring was continued for another minute. The precipitate was allowed to settle for one hour and then filtered through ashless filter paper. The precipitate was washed several times using a total of at least 150 mL of distilled water. The filter paper was transferred to a tared crucible, which was placed in an 800°C muffle furnace for ignition. After two hours the crucible was cooled and weighed. The weight of sulfur as sulfate in the pyrolysis solids was calculated by dividing the weight of sulfur found in this analysis by the fraction of pyrolysis solids used for the analysis.

THIOSULFATE AND SULFITE

The solid sample was weighed into a 100-mL volumetric flask containing 20 mL of freshly prepared $ZnCO_3$ suspension (10 mL 1N $NaCO_3$ + 10 mL 1N $ZnSO_4$). The solution

was mixed well and diluted to 100 mL. The suspension was filtered with quantitative grade filter paper.

Fifteen milliliters of filtrate were added to 10 mL 0.1N standard iodate-iodide solution and acidified with 10 mL 1N HCl. The solution was back-titrated with 0.1N standard $Na_2S_2O_3$ using a starch indicator. This gave $SO_3^=$ and $S_2O_3^=$.

Fifteen milliliters of filtrate were added to 15 mL 37% formaldehyde solution and allowed to stand for at least 5 minutes. Ten milliliters of 0.1N IO_3^--I^- solution were added and the solution was acidified with 10 mL 1N HCl. This was back-titrated with 0.1N $Na_2S_2O_3$ with a few drops of starch indicator to give the $Na_2S_2O_3$ concentration. The amount of sulfite was obtained by difference of the two numbers.

SULFIDE

The pyrolysis sample was added to SAOB II solution and tightly stoppered for storage.

For analysis, 1 g of Na_2SO_3 was added to the sample. The sample was then titrated with 0.1N standard $Cd(NO_3)_2$ solution using a sulfide specific ion electrode and a double junction reference electrode.

POLYSULFIDE

The sample was weighed into 20 mL of water and 5 g Na_2SO_3 in a beaker. The solution was heated without boiling for about 30 minutes. The solution was then analyzed for thiosulfate, as previously discussed.

The polysulfide was equal to one-half the newly found thiosulfate sulfur.

UNEXTRACTABLE SULFUR

After leaching of the solid residue with hot water and organic solvents, some sulfur remained as confirmed by x-ray analysis. This sulfur was either chemically bound or strongly adsorbed but was called organic sulfur here because it was associated with the organic residue.

GAS ANALYSIS

The gas samples collected during pyrolysis were analyzed by gas chromatography using a Perkin Elmer Sigma 2 gas chromatograph with a flame photometric detector. The detector was operated with a 394-nm filter. A Sigma 10 data system was used for peak area measurement and retention times. The column was an 18-inch Teflon tube 1/8 inch o.d., packed with 80/100 mesh acetone washed Porapak QS.

COLUMN PREPARATION AND CONDITIONING

Two grams of 80/100 mesh Porapak QS column packing were placed in a fine sintered glass funnel and washed for 5-10 minutes under suction with jets of pure acetone (70). The material was then allowed to dry under suction until free flowing. An 18-inch Teflon tube 1/8 inch in diameter was rinsed with acetone and dried. This tube was lightly packed with the acetone-washed Porapak QS by the vibration technique to an effective packed length of 12 inches. Glass wool plugs in both ends held the packing.

The column was conditioned overnight in an oven at 240°C with a nitrogen carrier gas flow rate of 30 cm^3/minute.

ANALYSIS CONDITIONS

The column temperature for analysis was programmed to start at 30°C, with a postinjection delay of 1 minute and then a 40°C/minute rise to 210°C. Nitrogen was

used as the carrier gas at a flow rate of 30 cm^3/minute. The injector temperature was 40°C, with a detector temperature of 115°C.

The syringes were Pressure-Lok Series A-2, treated with Prosil-28, an organosilane surface treating agent.

Response factor curves for the sulfur gases of interest - H_2S, COS, SO_2, and CH_3SH - were obtained by injection of sulfur gas samples diluted to the 0-100 ppm range. A graph of peak area vs. moles sulfur was constructed for each gas.

The Porapak QS column did not separate CS_2 and $(CH_3)_2S$. A 20-foot Carbowax 1500 column using a 70°C isothermal analysis was used to separate these two compounds and corroborate the previous identifications of unknowns by retention time.

VOLATILES DETERMINATION FROM ORGANIC STARTING MATERIALS

Crude volatiles determinations were performed on selected pyrolysis systems. Sample mixtures were pyrolyzed quickly in a muffle furnace at 550°C. The resulting char was cooled, leached with 200 mL hot water in a slow filter paper, and dried for one hour at 105°C. The amount of volatiles formed was determined by difference of the initial weight and the residual char weight.

VERIFICATION OF ANALYTICAL METHODS

Several of the analytical methods were thought to be potential problem areas. Of specific concern were possible losses of H_2S from Na_2S or SO_2 from Na_2SO_3 and $Na_2S_2O_3$ during the acidification step of the total sulfur analysis. Also of interest was whether or not $Na_2S_2O_3$ and Na_2SO_3 might appear in the sulfate analyses. The final question was whether or not the described methods were applicable to pyrolysis char samples.

TOTAL SULFUR ANALYSIS

Anhydrous Na_2SO_3, $Na_2S_2O_3$, and Na_2SO_4 were dryed for several hours at 105°C. The materials were cooled in a desiccator and weighed out. The samples were then treated with 5 mL of 32% H_2O_2 solution. A single large crystal of $Na_2S \cdot 9H_2O$ was cleaned with jets of distilled water from a wash bottle, dried in a paper towel, and then ground with mortar and pestle. Samples (2-10 millimoles) were quickly weighed and treated with the peroxide solution. The results were as follows:

	% Recovery
Na_2SO_4:	1) 101.0
	2) 102.4
Na_2SO_3:	1) 102.0
	2) 102.3
$Na_2S_2O_3$:	1) 101.4
	2) 102.0
Na_2S:	1) 100.6
	2) 100.4

These results indicate that there was no loss of sulfur from any of the salts during the acidification step when the hydrogen peroxide pretreatment was used.

SULFATE ANALYSIS

Standards for the sulfate analyses were obtained by pipetting 10 or 25 mL of an Acculute 0.1N H_2SO_4 solution into three beakers. These were then analyzed for sulfate by the described procedure. The results are as follows:

at 0.5 mm $SO_4^=$:	1)	0.1082 g $BaSO_4$
	2)	0.0964 g
	3)	0.1077 g

mean = 0.1041 = 89.2% recovery $SO_4^=$ (0.0143 g S)

at 1.25 mm $SO_4^=$: 1) 0.2979 g $BaSO_4$

2) 0.2951 g

3) 0.2966 g

mean = 0.2965 = 101.7% recovery $SO_4^=$ (0.0407 g S)

To verify that $Na_2S_2O_3$ would not appear in the sulfate analysis, 1.0 mm of a $Na_2S_2O_3$ standard solution was run through the sulfate analysis. The results were:

1) 0.0029 g $BaSO_4$

2) 0.0032 g

3) 0.0031 g

mean = 0.00307 = 0.67% recovery of S

The results indicated that the sulfate recovery depended on the amounts of sulfate present, suggesting that at low levels of sulfate, the analyses might underestimate the amount present. The results of the sulfate analyses starting with $Na_2S_2O_3$ indicated that neither thiosulfate nor sulfite would interfere with this test.

SULFIDE ANALYSIS

A single large crystal of $Na_2S \cdot 9H_2O$ was cleaned with small amounts of distilled water and then dried in a paper towel. This crystal was then crushed by mortar and pestle. Samples were weighed and analyzed by the described method. The results were:

1) 99.0% recovery of S

2) 98.3% recovery of S

This analytical procedure appeared adequate. No oxidation of sulfide stored in the SAOB II solution was indicated.

CHAR SULFUR ANALYSIS

The remaining question was whether or not the described analytical procedures could be used on a pyrolysis char. A large single sample of pyrolysis char was produced by several pyrolyses of sodium thiosulfate with sodium gluconate. All the separate char samples were mixed together and stored over P_2O_5 in a vacuum desiccator. Samples were removed under a nitrogen atmosphere for analysis. The results are presented in the table below:

PYROLYSIS OF $Na_2S_2O_3$ + SODIUM GLUCONATE

	Mean	Deviation	C. V., %	No. Tests	% Total
Total sulfur	0.1653	0.0051	3.1	4	100
S^o(Polysulfur)	0.0698	0.0047	6.8	3	42.2
$SO_4^=$	0.0369	0.0035	9.5	4	22.2
$SO_3^=$	0.0004	0.0003	75.0	4	0.2
$S_2O_3^=$	0.0028	0.0006	21.4	4	1.7
$S^=$	0.0621	0.0017	2.7	4	37.5
					103.8

The results indicate good precision in general; however, the precision for the $SO_3^=$ and $S_2O_3^=$ was poor. This could be explained by the low amounts present. It did not amount to a significant error in the sulfur balance. The good closure of the solid sulfur balance suggested good accuracy for the individual tests. No significant problems were indicated.

CONCLUSIONS

It was concluded that there would be no major problems with the application of the analytical methods to the char sulfur analyses. However, with later pyrolyses, some anomalies did appear in the char sulfur analyses. Specifically, there appeared to be problems with the solid sulfur analysis for the pyrolysis chars of sodium

gluconate with sodium sulfite or sodium sulfate (see Appendix II). It is most probable that these small errors are due to experimental error. However, since the anomalies appeared primarily with the sodium gluconate char, it is possible that this char might have interfered with the total sulfur analyses. These problems were not pursued, because the pyrolyses of sulfite and sulfate did not lead to significant volatile sulfur and, therefore, did not warrant further study. In conclusion, the overall results indicated that the total sulfur analyses were accurate and would not greatly affect sulfur balance closure.

APPENDIX II

EXPERIMENTAL RESULTS - TABULATED

The average sulfur recovery for the pyrolysis recorded in Appendix I is 98%. The residue sulfur composition was reproducible from one pyrolysis to another. During calibration of the flame photometric detector, it was found that the gases readily adsorbed on the container walls. The pyrolysis gas analysis results depended upon the length of time that the gases remained in collection bags before analysis. It is also probable that the other pyrolysis gases impeded proper response of the flame photometric detector used in the gas chromatographic analysis.

The poor gaseous sulfur recovery did not pose a problem. The amount of sulfur volatilized could be calculated as the difference in initial sulfur and total solid phase sulfur. This number depending on fewer measurements than calculation of the volatilized sulfur from FPD response factors and nitrogen flow rates would involve fewer sources of error. In the instances where several gases were significant, the relative gas composition did not change with recovery, as shown in Table IX.

All values listed in the following data for sulfur products are given as the percentage of initial sulfur. The organic materials are indicated as follows:

Sodium gluconate = G

Vanillic acid = V

Pyrolysis I.D. number	38	39	40	44
Materials pyrolyzed				
Inorganic	$Na_2S_2O_3$	$Na_2S_2O_3$	$Na_2S_2O_3$	$Na_2S_2O_3$
Organic	G	G	G	G
Inorganic particle mesh size	45-100	45-100	28-45	28-45
Initial conditions				
Heating rate, °C/min	13	13	13	13
N_2 Purge rate, cm^3/sec	16.25	16.25	16.25	16.25
Grams sulfur	0.2024	0.2009	0.2030	0.2033
Grams organic	2.5013	2.5125	2.5088	2.5003
Grams starting materials	3.0012	3.0085	3.0100	3.0022
Grams pyrolysis solids	1.4310	1.4051	1.4278	1.4320
Sulfur product distribution				
Solid phase				
$S^=$, %	40.91	42.46	35.75	36.60
S^o_x	12.56	13.14	23.94	18.30
$S_2O_3^=$	0.00	0.00	0.00	0.56
$SO_3^=$	0.94	1.29	3.27	2.36
$SO_4^=$	2.17	4.81	14.89	15.20
Total Sulfur, %	70.00	69.11	80.54	79.91
Condensable sulfur	--	--	--	--
Gas phase				
H_2S, %	9.17	8.00	4.14	6.76
COS	0.39	0.53	0.31	0.59
SO_2	1.35	3.07	1.40	2.16
CH_3SH	0.24	0.43	0.21	0.30
Other (as H_2S)	0.42	0.48	0.26	0.45
Total sulfur recovery	81.6	81.6	86.9	90.2

Pyrolysis I.D. number	45	47	49
Materials pyrolyzed			
Inorganic	$Na_2S_2O_3$	$Na_2S_2O_3$	$Na_2S_2O_3$
Organic	G	G	--
Inorganic particle mesh size	28-45	45-100	45-100
Initial conditions			
Heating rate, °C/min	23	23	13
N_2 Purge rate, cm^3/sec	16.25	16.25	16.25
Grams sulfur	0.2029	0.1624	1.2275
Grams organic	2.5072	2.5077	--
Grams starting materials	3.0081	2.9086	3.0306
Grams pyrolysis solids	1.5263	1.3813	2.6692
Sulfur product distribution			
Solid phase			
$S^=$, %	29.42	31.84	13.30
SO_x	16.46	9.40	29.40
$S_2O_3^=$	0.0	0.0	0.0
$SO_3^=$	1.55	0.49	1.0
$SO_4^=$	24.61	4.37	33.8
Total Sulfur, %	78.15	66.63	(77.5)
Condensable sulfur	--	--	
Gas phase			
H_2S, %	8.00	18.53	0.2
COS	0.53	0.80	0.0
SO_2	8.55	13.24	5.3
CH_3SH	0.30	0.91	--
Other (as H_2S)	0.38	1.50	0.2
Total sulfur recovery	95.9	101.6	83.2

Pyrolysis I.D. number	52	54	55	56
Materials pyrolyzed				
Inorganic	$Na_2S_2O_3$	$Na_2S_2O_3$	$Na_2S_2O_3$	$Na_2S_2O_3$
Organic	G	G	V	V
Inorganic particle mesh size	45-100	45-100	45-100	45-100
Initial conditions				
Heating rate, °C/min	13	13	13	13
N_2 Purge rate, cm^3/sec	29.75	12.0	31.75	12.0
Grams sulfur	0.2023	0.2042	0.2041	0.2037
Grams organic	2.5012	2.4969	2.5102	2.4986
Grams starting materials	3.0006	3.0010	3.0051	3.0015
Grams pyrolysis solids	1.4431	1.4139	0.3812	0.3844
Sulfur product distribution				
Solid phase				
$S^=$, %	39.55	37.92	29.61	--
S^o_x	10.86	12.99	--	--
$S_2O_3^=$	0.0	0.0	--	--
$SO_3^=$	2.72	1.57	--	--
$SO_4^=$	4.55	4.71	--	--
Total Sulfur, %	71.67	68.66	55.56	54.59
Condensable sulfur	0.55	0.78	1.31	--
Gas phase				
H_2S, %	17.10	11.88	3.71	3.01
COS	0.63	0.59	0.15	0.32
SO_2	3.61	1.91	10.53	18.41
CH_3SH	1.04	0.86	2.68	2.98
Other (as H_2S)	0.89	0.58	3.91	5.89
Total sulfur recovery	95.5	85.3	77.9	85.2

Pyrolysis I.D. number	50	51	57	58
Materials pyrolyzed				
Inorganic	$Na_2S_2O_3$	$Na_2S_2O_3$	$Na_2S_2O_3$	$Na_2S_2O_3$
Organic	V	V	V	V
Inorganic particle mesh size	45-100	45-100	28-45	28-45
Initial conditions				
Heating rate, °C/min	13	23	13	23
N_2 Purge rate, cm^3/sec	16.25	16.25	16.25	16.25
Grams sulfur	0.2038	0.2078	0.2033	0.2046
Grams organic	2.4975	2.4958	2.4955	2.5002
Grams starting materials	3.0006	3.0088	2.9974	3.0053
Grams pyrolysis solids	0.3683	0.3959	0.3758	0.3804
Sulfur product distribution				
Solid phase				
$S^=$, %	32.30	26.87	31.60	31.60
SO_x	--	--	--	--
$S_2O_3^=$	--	--	--	--
$SO_3^=$	--	--	--	--
$SO_4^=$	--	--	--	--
Total Sulfur, %	57.46	56.34	65.81	68.59
Condensable sulfur	7.64	8.28	1.87	1.56
Gas phase				
H_2S, %	5.98	5.79	3.86	3.50
COS	0.10	0.50	0.10	0.31
SO_2	27.32	26.53	17.82	15.07
CH_3SH	2.94	2.73	2.28	1.28
Other (as H_2S)	5.57	4.84	4.22	3.21
Total sulfur recovery	107.0	105.0	96.0	93.5

Pyrolysis I.D. number	59	60	61	62
Materials pyrolyzed				
Inorganic	Na_2SO_4	Na_2SO_4	Na_2SO_4	Na_2SO_4
Organic	G	G	V	V
Inorganic particle mesh size	45-100	45-100	45-100	45-100
Initial conditions				
Heating rate, °C/min	13	23	13	23
N_2 Purge rate, cm^3/sec	26.0	26.0	16.25	16.25
Grams sulfur	0.2028	0.2035	0.2026	0.2027
Grams organic	2.5064	2.4963	2.5053	2.5125
Grams starting materials	3.4063	3.3993	3.404	3.4120
Grams pyrolysis solids	2.0010	1.9945	1.1357	1.1105
Sulfur product distribution				
Solid phase				
$S^=$, %	0.0	0.0	0.0	0.0
S^o_x	0.0	0.0	0.0	0.0
$S_2O_3^=$	0.0	0.0	0.0	0.0
$SO_3^=$	0.0	0.0	0.0	0.0
$SO_4^=$	93.75	91.93	107.2	106.8
Total Sulfur, %	103.0	101.1	107.2	107.2
Condensable sulfur	0.74	0.86	0.0	0.0
Gas phase				
H_2S, %	0.54	0.24	0.14	0.15
COS	0.05	trace	0.05	trace
SO_2	2.02	4.52	1.13	0.20
CH_3SH	0.20	0.0	0.39	0.0
Other (as H_2S)	0.39	0.29	0.0	0.05
Total sulfur recovery	106.9 (97.7)	107.0 (97.8)	108.9	107.6

Pyrolysis I.D. number	63	64	66	65
Materials pyrolyzed				
Inorganic	Na_2SO_3	Na_2SO_3	Na_2SO_3	Na_2SO_3
Organic	G	G	V	V
Inorganic particle mesh size	45-100	45-100	45-100	45-100
Initial conditions				
Heating rate, °C/min	13	23	13	23
N_2 Purge rate, cm^3/sec	26.0	26.0	16.25	16.25
Grams sulfur	0.1976	0.1980	0.2000	0.1991
Grams organic	2.5039	2.5026	2.4966	2.5320
Grams starting materials	3.2820	3.2822	3.2841	3.3160
Grams pyrolysis solids	1.8708	1.8690	0.8110	0.8060
Sulfur product distribution				
Solid phase				
$S^=$, %	0.0	0.0	0.0	0.0
SO_x	0.0	0.0	0.0	0.0
$S_2O_3^=$	0.0	0.0	0.0	0.0
$SO_3^=$	100.2	100.8	87.40	86.83
$SO_4^=$	0.0	0.0	0.0	0.0
Total Sulfur, %	93.47	97.02	91.35	89.65
Condensable sulfur	0.0	0.0	0.0	1.26
Gas phase				
H_2S, %	0.0	0.0	0.0	0.05
COS	0.0	0.0	0.0	trace
SO_2	0.0	0.0	7.45	8.34
CH_3SH	0.0	0.0	0.10	0.10
Other (as H_2S)	0.0	0.0	0.35	0.20
Total sulfur recovery	93.47	97.02	99.23	99.60

Pyrolysis I.D. number	69	70	71	72
Materials pyrolyzed				
Inorganic	Na_2S	Na_2S	Na_2S	Na_2S
Organic	V	V	V	V
Inorganic particle mesh size	28-45	28-45	45-100	45-100
Initial conditions				
Heating rate, °C/min	13	23	13	23
N_2 Purge rate, cm^3/sec	16.25	16.25	16.25	16.25
Grams sulfur	0.2001	0.2006	0.2008	0.1997
Grams organic	2.5090	2.5004	2.4824	2.4962
Grams starting materials				
Grams pyrolysis solids	1.1184	1.0760	1.0732	1.0281
Sulfur product distribution				
Solid phase				
$S^=$, %	1.83	2.07	1.88	2.51
SO_x	--	--	--	--
$S_2O_3^=$	0.0	0.0	0.0	0.0
$SO_3^=$	0.0	0.0	0.0	0.0
$SO_4^=$	0.0	0.0	0.0	0.0
Total Sulfur, %	2.45	3.45	3.49	4.67
Condensable sulfur	0.89	1.45	0.43	2.38
Gas phase				
H_2S, %	97.75	62.21	99.70	79.97
COS	trace	0.50	0.35	trace
SO_2	0.0	0.0	trace	0.40
CH_3SH	0.95	1.30	2.64	6.76
Other (as H_2S)	2.85	2.99	3.49	4.51
Total sulfur recovery	104.9	71.9	110.1	98.7

Pyrolysis I.D. number	73	74	75	76
Materials pyrolyzed				
Inorganic	Na_2S	Na_2S	Na_2S	Na_2S
Organic	G	G	G	G
Inorganic particle mesh size	28-45	28-45	45-100	45-100
Initial conditions				
Heating rate, °C/min	13	23	13	23
N_2 Purge rate, cm^3/sec	26.0	26.0	26.0	26.0
Grams sulfur	0.1859	0.2023	0.1992	0.2001
Grams organic	2.4993	2.5065	2.5078	2.5054
Grams starting materials				
Grams pyrolysis solids	1.8947	1.9414	1.9668	1.9546
Sulfur product distribution				
Solid phase				
$S^=$, %	5.70	4.00	5.63	3.08
SO_x	--	--	--	--
$S_2O_3^=$	0.0	0.0	0.0	0.0
$SO_3^=$	0.0	0.0	0.0	0.0
$SO_4^=$	0.0	0.0	0.0	0.0
Total Sulfur, %	10.67	8.94	11.30	9.26
Condensable sulfur	--	--	--	--
Gas phase				
H_2S, %	111.0	75.5	67.45	59.97
COS	trace	0.0	trace	0.0
SO_2	0.80	2.67	0.8	2.05
CH_3SH	0.22	0.40	0.0	0.0
Other (as H_2S)	0.32	0.25	0.10	0.0
Total sulfur recovery	123.0	87.8	79.7	71.28

Pyrolysis I.D. number	77	79	80
Materials pyrolyzed			
Inorganic	Na_2SO_3 + S^o	Na_2SO_3 + S^o	$Na_2S_2O_3$
Organic	G	V	V
Inorganic particle mesh size	45-100	45-100	45-100
Initial conditions			
Heating rate, °C/min	23	23	13
N_2 Purge rate, cm^3/sec	26.0	20.25	20.25
Grams sulfur	0.1004 S^o	0.1062 S^o	
	0.1017 SO_3	0.1050 SO_3	0.2018
Grams organic	2.5100	2.5067	2.5061
Grams starting materials	3.0107	3.0262	3.0043
Grams pyrolysis solids	1.5439	0.4689	0.3845
Sulfur product distribution			
Solid phase			
$S^=$, %	0.0	Present	--
S^o_x	--	--	35.0
$S_2O_3^=$	--	--	--
$SO_3^=$	--	--	--
$SO_4^=$	--	--	2.1
Total Sulfur, %	54.7	45.0	--
Condensable sulfur	--	8.8	--
Gas phase			
H_2S, %	12.85	6.25	--
COS	0.20	0.14	--
SO_2	1.86	7.86	--
CH_3SH	0.80	4.50	--
Other (as H_2S)	--	4.4	--
Total sulfur recovery	70.4	77.0	--

APPENDIX III

STATISTICAL ANALYSIS OF DATA

Regression analysis of the raw data in Appendix II was carried out to obtain the amount of total solid phase sulfur as a function of the various parameters:

$y = F(X_1, X_2, X_3, X_4, X_5, X_6)$

y = amount of total solid phase sulfur (as percentage of initial sulfur)

X_1 = particle size range (36.5 or 72.5)

X_2 = heating rate (13 or 23)

X_3 = sodium gluconate (1 or 0)*

X_4 = presence of Na_2S (1 or 0)

X_5 = presence of $Na_2S_2O_3$ (1 or 0)

X_6 = presence of Na_2SO_3 (1 or 0)

The presence of Na_2SO_4 was implied by the lack of Na_2S, $Na_2S_2O_3$ and Na_2SO_3.

The function obtained had the form:

$$y = a_0 + a_1X_1 + a_2X_2 + \ldots + a_6X_6$$

	Calculated Value	Standard Error	T
a_0	0.114799×10^3	--	--
a_1	-0.182717	0.54847×10^{-1}	3.331
a_2	-0.419478×10^{-1}	0.172272	0.243
a_3	0.758814×10^1	0.164800×10^1	4.604
a_4	-0.100789×10^3	0.291938×10^1	34.524
a_5	-0.399097×10^2	0.267569×10^1	14.916
a_6	-0.115000×10^2	0.317240×10^1	3.625

Correlation coefficient $r^2 = 0.99$

*The lack of sodium gluconate implies the presence of vanillic acid.

ANALYSIS OF VARIANCE TABLE

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square
Regression	6	3.6217×10^4	6.036×10^3
Residual	23	4.6295×10^2	20.13
Total	29	3.66799×10^4	

Standard deviation = $\sqrt{20.13}$

$$s = 4.49$$

$$\text{Confidence interval (C.I.)} = \bar{y} \pm \frac{ts}{\sqrt{N}}$$

't' for 95% confidence interval (±0.025) with 23 degrees of freedom = 2.069

Therefore C.I. = $\bar{y} \pm \frac{9.29}{\sqrt{N}}$

Pyrolysis	Mean Total Sulfur	Number of Points	95% Confidence Interval
$Na_2S_2O_3$ + G	73.08	8	69.8 to 76.4
$Na_2S_2O_3$ + V	59.73	6	55.9 to 63.5
Na_2SO_4 + G	102.05	2	95.5 to 108.6
Na_2SO_4 + V	107.2	2	100.6 to 113.8
Na_2SO_3 + G	95.25	2	88.7 to 101.8
Na_2SO_3 + V	90.50	2	83.9 to 97.1
Na_2S + G	10.04	4	5.4 to 14.7
Na_2S + V	3.52	4	-1.1 to 8.2

Sodium gluconate = G

Vanillic acid = V

Results of the statistical analysis:

1) Heating rate was not an important pyrolysis variable under the conditions employed.

2) There was a statistically significant difference in the amount of sulfur volatilized (100.0% - total solid sulfur) from $Na_2S_2O_3$ when pyrolyzed with sodium gluconate or vanillic acid.

3) There was no statistically significant volatilization of sulfur during the pyrolysis of Na_2SO_3 with sodium gluconate. However, there was a statistically significant amount of sulfur volatilized during pyrolysis of Na_2SO_3 with vanillic acid.

4) There was no statistically significant volatilization of sulfur from the Na_2SO_4 based on solid phase analyses. However, it should be noted that small amounts of sulfur gases were observed by gas chromatography during pyrolysis of the Na_2SO_4.

APPENDIX IV

THIOSULFATE PYROLYSIS SULFUR-GAS TIME SEQUENCE

Pyrolysis	Organic	Heating Rate, °C/min	Time, min	Relative Peak Areas H_2S	Relative Peak Areas SO_2
38	G	13	0-30	6.9	--
			30-60	52.0	7.4
39	G	13	0-30	17.3	2.5
			30-60	34.9	14.3
40	G	13	0-30	2.67	0.2
			30-60	20.9	7.8
44	G	13	0-30	5.0	1.5
			30-60	39.4	10.68
45	G	23	0-30	53.0	12.0
			30-60	1.3	20.7
47	G	23	0-30	50.0	13.9
			30-60	0.24	11.4
52	G	13	0-20	--	0.5
			20-37	45.1	5.4
			37-57	27.0	10.48
			57-74	0.3	1.6
54	G	13	0-20	--	0.4
			20-40	43.4	4.0
			40-60	65.8	10.6
			60-81	--	3.2
55	V	13	0-15	--	--
			15-32	4.5	23.0
			32-49	5.9	2.5
			49-60	0.5	1.4
			60-75	--	0.3
56	V	13	0-20	--	--
			20-40	12.6	27.4
			40-61	6.6	14.1
			61-76	0.1	3.1
50	V	13	0-30	0.2	36.2
			30-60	37.2	63.9
			60-87	0.3	4.2
			87-120	0.2	0.6

APPENDIX IV (Continued)

Pyrolysis	Organic	Heating Rate, °C/min	Time, min	Relative Peak Areas H_2S	Relative Peak Areas SO_2
51	V	23	1-30	37.6	115.8
			30-60	0.6	34.1
			60-90	--	1.76
57	V	13	0-21	--	--
			21-40	26.7	139.4
			40-61	11.7	13.1
			61-76	0.1	1.9
58	V	23	1-10.5	30.8	155.1
			10.5-31.0	18.2	13.4
			31-60	0.2	24.5
			60-74	--	4.4

The percentage of H_2S or SO_2 formed during each time interval can be calculated by dividing the relative peak area for the time interval considered by the sum of all the relative peak areas for that gas during the pyrolysis and multiplying the result by 100%. For example, during pyrolysis 38,

$$\frac{6.9}{52.0 + 6.9} \times 100\%$$

of the H_2S was volatilized between 0 and 30 minutes.

$Na_2S_2O_3$ + SODIUM GLUCONATE

Both H_2S and SO_2 appeared during first 30 minutes of pyrolysis; 25-390°C.

$Na_2S_2O_3$ + VANILLIC ACID

A large percentage of the SO_2 was produced between 25 and 260°C. This occurred occasionally with small amounts of H_2S. The principal portions of H_2S were produced above 260°C.

These results support the reaction model for thiosulfate during pyrolysis. If sulfur dioxide were produced by an acidic decomposition of the thiosulfate as suggested, this reaction would be expected to occur early in the pyrolysis. This table does show that sulfur dioxide appeared early, usually preceding H_2S. This is especially apparent for the vanillic acid pyrolyses.